GUIDANCE DOCUMENT

Field Demonstration, Optimization, and Rigorous Validation of Peroxygen-Based ISCO for the Remediation of Contaminated Groundwater - CHP Stabilization Protocol

ESTCP Project ER-200632

May 2014

Richard Watts
Amy Teel
Washington State University

Richard Brown
Tim Pac
ERM Inc.

ESTCP

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
MAY 2014		**00-02-2007 to 00-01-2014**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Field Demonstration, Optimization, and Rigorous Validation of Peroxygen-Based ISCO for the Remediation of Contaminated Groundwater - CHP Stabilization Protocol	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Washington State University,Pullman,WA,99163-2910**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Catalyzed H2O2 propagations (CHP) is the in situ chemical oxidation (ISCO) process with the most robust chemistry and potential for contaminant destruction. However, hydrogen peroxide is unstable in the subsurface and as a result, CHP use has decreased in favor of activated persulfate as an ISCO reagent. Recent advances have been made in stabilizing hydrogen peroxide in the presence of subsurface solids. The addition of sodium citrate, sodium malonate, and sodium phytate can potentially slow hydrogen peroxide decomposition rates by up to 50 fold. The optimal implementation of these stabilizers for use in CHP field applications is detailed in this guidance document.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**	**Same as Report (SAR)**	**99**	

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED** *(From - To)*
24-01-2014	Special	Feb 2007 – Jan 2014

4. TITLE AND SUBTITLE
Field Demonstration, Optimization, and Rigorous Validation of Peroxygen-Based ISCO for the Remediation of Contaminated Groundwater - CHP Stabilization Protocol

5a. CONTRACT NUMBER
W912HQ-07-C-0003

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Watts, Richard J.; Teel, Amy L.; Brown, Richard A.; Pac, Tim

5d. PROJECT NUMBER
ER-200632

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Washington State University
Pullman, WA, 99163-2910

ERM
250 Phillips Blvd., Suite 280
Ewing NJ 08618

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Environmental Security Technology Certification Program

10. SPONSOR/MONITOR'S ACRONYM(S)
ESTCP

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Catalyzed H_2O_2 propagations (CHP) is the in situ chemical oxidation (ISCO) process with the most robust chemistry and potential for contaminant destruction. However, hydrogen peroxide is unstable in the subsurface and as a result, CHP use has decreased in favor of activated persulfate as an ISCO reagent. Recent advances have been made in stabilizing hydrogen peroxide in the presence of subsurface solids. The addition of sodium citrate, sodium malonate, and sodium phytate can potentially slow hydrogen peroxide decomposition rates by up to 50 fold. The optimal implementation of these stabilizers for use in CHP field applications is detailed in this guidance document.

15. SUBJECT TERMS
In situ chemical oxidation; catalyzed H2O2 propagations; stabilization

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			**19b. TELEPHONE NUMBER** *(include area code)*

Table of Contents

List of Acronyms

BDST	Bed depth service time
CHP	Catalyzed H_2O_2 propagations
CoCs	Contaminants of concern
GC	Gas chromatography
DNAPL	Dense nonaqueous phase liquid
ISCO	In situ chemical oxidation
HCA	Hexachloroethane
ICS	Iron-coated sand
LC	Liquid chromatography
MCS	Manganese-coated sand
NAPL	Nonaqueous phase liquid
ORP	Oxidation reduction potential
PAHs	Polycyclic aromatic hydrocarbons
PCE	Tetrachloroethylene
PFC	Perfluorinated compound
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonate
RI/FS	Remedial investigation/feasibility study
SOD	Soil oxidant demand
TCE	Trichloroethylene
TPH	Total petroleum hydrocarbon
TOC	Total organic carbon
VOA	Volatile organic analysis
VOCs	Volatile organic compounds

List of Figures

List of Tables

Acknowledgements

The Principal Investigators would like to thank the graduate students and postdoctoral researchers who have worked on the project including Robert Vaughan, Jeremiah Trnka, and Mushtaque Ahmad. We would also like to thank the ESTCP program manager, Dr. Andrea Leeson, and the ESTCP staff for assistance and support throughout the project.

Executive Summary

Catalyzed H_2O_2 propagations (CHP) is the in situ chemical oxidation (ISCO) process with the most robust chemistry and potential for contaminant destruction. Because it generates high fluxes of hydroxyl radical, superoxide radical, and hydroperoxide anion, CHP can destroy nearly all environmental contaminants of concern and provide enhanced treatment of sorbed contaminants and nonaqueous phase liquids (NAPLs). However, hydrogen peroxide is unstable in the subsurface and as a result, CHP use has decreased in favor of activated persulfate as an ISCO reagent.

Recent advances have been made in stabilizing hydrogen peroxide in the presence of subsurface solids. The addition of sodium citrate, sodium malonate, and sodium phytate can potentially slow hydrogen peroxide decomposition rates by up to 50 fold. The optimal implementation of these stabilizers for use in CHP field applications is detailed in this guidance document.

Multi-tiered treatability studies are outlines in the guidance document. The first step in treatability studies is the evaluation of stabilized and unstabilized hydrogen peroxide decomposition rates. The optimum hydrogen peroxide concentration and stabilizer concentration are then used in field implementation.

This guidance manual then outlines field development of stabilized CHP. Field conditions, site conditions, and health and safety issues are addressed. The guidance document concludes with detailed descriptions of two case histories.

1 Introduction to Catalyzed H_2O_2 Propagations

In situ chemical oxidation (ISCO) is the delivery of strong chemical oxidants to the subsurface for the purpose of treating organic contaminants. In the 1990s, the first reports were published on ISCO (Watts et al., 1990; Schnarr and Farquhar, 1992), and by the mid-1990s, specialty companies had been established that offered ISCO services almost exclusively. The first ISCO process that was investigated in laboratory research and developed at full scale was catalyzed H_2O_2 propagations (CHP), commonly known as modified Fenton's reagent (Watts et al., 1990; Tyre et al., 1991).

1.1 CHP Background

The use of CHP has become increasingly popular for the in situ and ex situ treatment of surface soils and the in situ remediation of the subsurface. CHP is based on Fenton's reagent, a laboratory procedure in which dilute hydrogen peroxide is slowly added to a solution of excess iron (II) to generate hydroxyl radical (OH•) (Walling, 1975):

$$H_2O_2 + Fe^{2+} \rightarrow OH\bullet + OH^- + Fe^{3+} \qquad k = 76\ M^{-1}\ s^{-1} \qquad (1\text{-}1)$$

However, much higher concentrations of hydrogen peroxide are used in CHP applications, as well as the use of alternative catalysts such as iron (III), iron chelates, and iron and manganese minerals (Watts and Teel, 2005).

1.1.1 Hydroxyl Radical Reactivity

The oxidant of interest in CHP has traditionally been hydroxyl radical, one of the strongest oxidants found in nature. The rate of reaction of hydroxyl radical with an organic compound (C) is described by the second-order rate expression:

$$-\frac{dC}{dt} = k[C][OH\bullet] \quad (1\text{-}2)$$

where k = the second order rate constant (M^{-1} s^{-1})

Chemicals that react very rapidly with hydroxyl radical are limited by the rate of diffusion of hydroxyl radical in water, which is $\approx 1 \times 10^{10}$ M^{-1} s^{-1}, rather than the rate at which it attacks the chemical. Therefore, the rate at which hydroxyl radical attacks highly reactive contaminants in aqueous systems is referred to as diffusion-controlled. Some general rules have been established for the reactivity of hydroxyl radical with organic contaminants. Second order rate constants $>10^9$ M^{-1} s^{-1} are considered high enough to be effective for ISCO treatments, while rate constants $<10^8$ M^{-1} s^{-1} are considered too low to be effective (Watts, 1998). Almost all aromatic compounds, even those with a high degree of halogenation, react rapidly with hydroxyl radical (Table 1-1). Chlorinated alkenes, such as trichloroethylene (TCE) and tetrachloroethylene (PCE), also react rapidly. In contrast, alkanes exhibit relatively low reactivity with hydroxyl radical; in particular, chlorinated and fluorinated alkanes such as carbon tetrachloride, chloroform, perfluorooctanoic acid (PFOA), and perfluorooctane sulfonate (PFOS) are essentially non-reactive.

Table 1-1. Second-Order Rate Constants for the Reactivity of Hydroxyl Radical with Common Contaminants

Compound	$k_{OH\bullet}$ (M^{-1} s^{-1})
Polycyclic Aromatic Hydrocarbons	1.0×10^{10}
Benzene	7.8×10^{9}
Ethylbenzene	7.5×10^{9}
Xylenes	7.0×10^{9}
Trichloroethylene (TCE)	4.0×10^{9}
Toluene	3.0×10^{9}
Tetrachloroethylene (PCE)	2.8×10^{9}
PFOA	$<1 \times 10^{6}$
PFOS	$<1 \times 10^{6}$

Sources: Chang and Young (2000); Haag and Yao (1992); Schmelling et al. (1998)

1.1.2 Non-Hydroxyl Radical Species

Under the conditions of high hydrogen peroxide concentrations used for CHP ISCO, hydroxyl radical generated in the Fenton's initiation reaction (reaction 1) reacts with hydrogen peroxide to promote a series of propagation reactions (Walling, 1975; Buxton et al., 1988):

$$OH\bullet + H_2O_2 \rightarrow HO_2\bullet + H_2O \qquad k = 2.7 \times 10^7\ M^{-1}\ s^{-1} \qquad (1\text{-}3)$$

$$HO_2\bullet \leftrightarrow O_2\bullet^- + H^+ \qquad pK_a = 4.8 \qquad (1\text{-}4)$$

$$R\bullet + H_2O_2 \rightarrow ROH + OH\bullet \qquad k = 10^6\text{–}10^8\ M^{-1}\ s^{-1} \qquad (1\text{-}5)$$

$$HO_2\bullet + Fe^{2+} \rightarrow HO_2^- + Fe^{3+} \qquad k = 1.2 \times 10^6\ M^{-1}\ s^{-1} \qquad (1\text{-}6)$$

Although the rate constant for reaction 1-3 is relatively low, these reactions become important when the concentration of hydrogen peroxide is high (e.g., > 1%). Therefore, the rates of generation of perhydroxyl radical ($HO_2\bullet$), superoxide radical anion ($O_2\bullet^-$), and hydroperoxide anion (HO_2^-) become significantly greater at higher hydrogen peroxide concentrations.

Hydroperoxide, the conjugate base of hydrogen peroxide (pK_a = 11.75), is a strong nucleophile (Edwards and Pearson, 1962; David and Seiber, 1999). Perhydroxyl radical is a weak oxidant that has minimal reactivity in aqueous systems (Afanas'ev, 1989). Superoxide is a nucleophile and a reductant that has been considered unreactive in aqueous systems, though it is highly reactive in aprotic solvents such as dimethyl sulfoxide and dimethyl formamide.

Although some of these species (e.g., superoxide) are not reactive in deionized water, their reactivity is significantly increased in systems that contain solutes such as hydrogen peroxide; the solutes provide a solvent effect, increasing the reactivity of superoxide (Smith et al., 2004). Not only do dissolved species, such as low-molecular weight solvents and hydrogen peroxide, promote increased reactivity of superoxide, but Furman et al. (2009) documented that solids, including minerals and soils, also increase superoxide reactivity. Such a phenomenon makes superoxide an especially attractive reactant in soils and the subsurface.

CHP reactions that generate hydroxyl radical, superoxide, and hydroperoxide provide a mixture of oxidants, reductants, and nucleophiles that can degrade almost all organic contaminants. For example, carbon tetrachloride and hexachloroethane, which are unreactive with hydroxyl radical, are rapidly degraded in CHP systems through reactions with superoxide in the presence of sufficient hydrogen peroxide to provide a solvent effect (Watts et al., 1999; Teel and Watts, 2002; Smith et al., 2004). Therefore, these reactive oxygen species increase the range of CHP reactivity, making CHP a near-universal treatment system.

1.1.3 CHP ISCO Process Conditions

Some of the important process parameters for CHP ISCO include the nature of the catalyst, the pH, and the hydrogen peroxide concentration. Soluble iron and iron chelates have

been used as CHP catalysts (Sun and Pignatello, 1992; Pignatello and Baehr, 1994). In addition, the iron oxide minerals naturally present in the subsurface serve as effective CHP catalysts (Tyre et al., 1991; Watts et al., 1993). The manganese oxide birnessite catalyzes CHP reactions that generate only superoxide, with no hydroxyl radical generation (Furman et al., 2009). The pH of CHP systems is an important process parameter. If soluble iron or iron minerals are used as the CHP catalyst, the pH must be maintained at less than pH 4. Reactions 1 and 3–6 are sensitive to oxidation-reduction conditions, and the acidic pH regime provides suitable redox conditions; in addition, the acidic conditions aid in maintaining soluble iron in solution. If iron chelates or manganese oxides are used as catalysts, the reactions can be conducted at neutral pH regimes. Hydrogen peroxide concentrations in the 2–12% (0.6–3.6 M) range are typically used for ISCO applications, and the common practice in the field has been to increase the concentration of hydrogen peroxide when treatment has been unsuccessful. This practice often enhances treatment effectiveness, in part because the high hydrogen peroxide concentration provides a pool of the oxidant source. More importantly, however, high hydrogen peroxide concentrations also promote the propagation reactions that 1) generate perhydroxyl radical, superoxide radical anion, and hydroperoxide anion (reactions 3–6), and 2) increase the reactivity of superoxide through a solvent effect.

1.1.4 Enhanced Treatment of Sorbed Contaminants and NAPLs

A distinct advantage of CHP over other ISCO processes is the documented enhanced treatment of sorbed contaminants and nonaqueous phase liquids (NAPLs). These contaminant states are problematic because almost all reactants used in soil and groundwater remediation (e.g., hydroxyl radical, reductants, bacteria) are present in the aqueous phase. Therefore, sorbed contaminants must desorb into the aqueous phase before transformation can occur. As the

contaminants are degraded in the aqueous phase, a concentration gradient increases between the sorbed phase and the aqueous phase, driving subsequent desorption (Watts et al., 1994). Similar dynamics occur in the treatment of NAPLs; the contaminant must dissolve into the aqueous phase before it is degraded (Yeh et al., 2003; Smith et al., 2004; Smith et al., 2006). Such treatment is referred to as desorption- or dissolution-limited, and can require years or even decades for site cleanup (Watts, 1998). However, superoxide generated in CHP reactions has the potential to treat sorbed contaminants and NAPLs at a rate significantly greater than the rate of desorption or dissolution (Smith et al., 2006; Corbin et al., 2007). In some cases, the rate of sorbed contaminant or NAPL destruction can be up to 100 times faster than the rate of desorption- or dissolution-limited treatment. These results have also been seen in the field; rapid treatment of sorbed contaminants and NAPLs using CHP has been demonstrated in numerous field studies (U.S. DOE, 1999).

1.2 Hydrogen Peroxide Stabilization

1.2.1 Instability of Hydrogen Peroxide

Although CHP is a near-universal treatment system that degrades any organic contaminant studied to date, it is characterized by a significant shortcoming: high rates of hydrogen peroxide decomposition in surface soils and the subsurface. The half life of hydrogen peroxide varies substantially in ISCO applications, ranging from a few hours to 10 days at its uppermost limit (ESTCP, 1999). Therefore, a disadvantage of CHP ISCO is that hydrogen peroxide is rapidly decomposed by minerals in the subsurface, limiting its transport and its contact with contaminants. Furthermore, hydrogen peroxide stability is the primary factor that determines injection well spacing at CHP treatment sites. The rate of hydrogen peroxide decomposition is used in conjunction with the pore water velocity to determine the radius of

influence for injection wells. If the hydrogen peroxide decomposition rate is slow, well centers are typically 25–30 feet (7.6–9.1 m); rapid hydrogen peroxide decomposition dictates injection wells on 5–10 foot (1.5–3.0 m) centers. Even though CHP provides a robust treatment chemistry capable of destroying nearly all contaminants of concern, the rapid decomposition of hydrogen peroxide often vastly reduces its effectiveness (Watts and Teel, 2006). Therefore, several methods have been studied for stabilizing hydrogen peroxide in the subsurface for ISCO. The addition of phosphate has been investigated, but its effect on hydrogen peroxide stability was minimal (Hinchee et al., 1991). Acidic pH regimes have been effective in reducing the rate of hydrogen peroxide decomposition in systems catalyzed by naturally occurring iron minerals, resulting in more effective treatment stoichiometry (Tyre et al., 1991; Ravikumar and Gurol, 1994; Miller and Valentine, 1995). This effect is likely due to the acidic pH dissolving the highly catalytic manganese oxides also present in the systems (Watts et al., 2005). A disadvantage of this method of stabilization is that acidification is difficult to implement in the field, and acidification of entire groundwater systems is generally considered impractical.

1.2.2 Organic Stabilizers

Recent studies have described additives that can effectively stabilize hydrogen peroxide in the presence of subsurface soils. Watts et al. (2007) screened 11 organic ligands for their potential to stabilize hydrogen peroxide. Of the 11 ligands, the organic acids citrate, malate, and phytate were the most effective. The structures of citrate, malate, and phytate are shown in Figure 1-1. Although the most effective stabilizer was found to be site specific, phytate was often the most effective, increasing hydrogen peroxide half-lives up to 800%. Furthermore, these stabilizing ligands did not scavenge reactive oxygen species, resulting in effective contaminant destruction. The effectiveness of hydrogen peroxide stabilization was confirmed by Schmidt et

al. (2011) in iron oxide- and manganese oxide-coated sand columns; unstabilized hydrogen peroxide migrated < 10 cm in the columns, while phytate-stabilized hydrogen peroxide was present at 120 cm down the column.

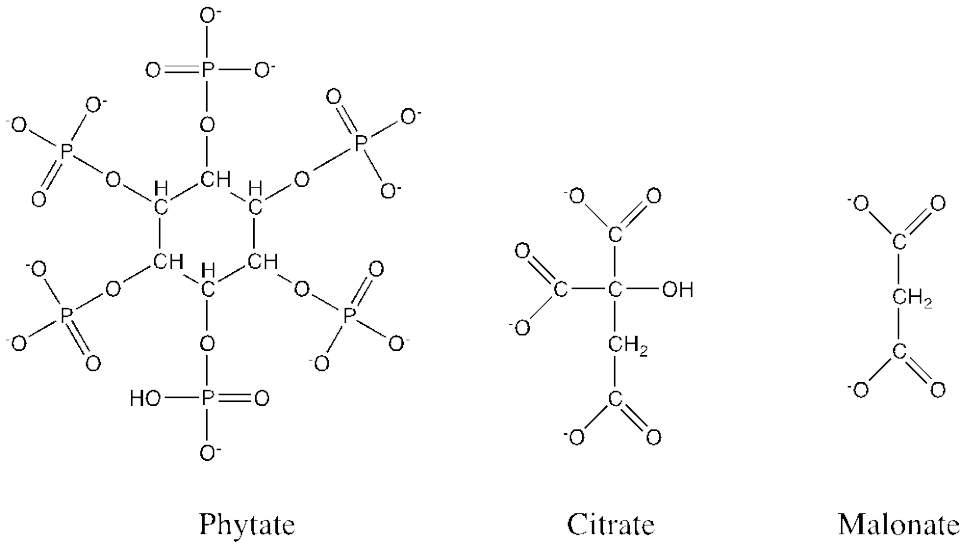


Figure 1-1. Structures of the stabilizers phytate, citrate, and malonate

The toxicity of citrate, malonate, and phytate is minimal. Citrate and malonate are biological intermediates in metabolism, and phytate is isolated from soybeans. However, the three stabilizer vary in price and availability. Phytate, the most expensive of the stabilizers, is available from Fabrichem, Inc., Trumbull, CT (fabrichem.com) for $59/kg for a 50% solution. Sodium citrate can be purchased from SoapGoods, Smyrna, GA (soapgoods.com). The cost is based on a sliding scale: the cost for a 50 pound order is $2.96/pound, while the cost for a 2000 pound order is $2.01/pound. Sodium malonate is less available than the other two stabilizers. It can be purchased from Sigma Aldrich (sigmaaldrich.com) at $300/pound.

Organic acids that chelate transition metals have previously been used to initiate CHP reactions. Sun and Pignatello (1992) screened over 30 organic acid–iron (III) complexes as CHP catalysts and found a wide range of activity. The low activity of some of the iron ligands is likely related to their high stability constants (Sheldon and Kochi, 1981); these ligands that strongly bind iron may also stabilize hydrogen peroxide in the presence of subsurface solids. The conceptual model for such stabilization is to add the sodium salt of the organic acid (e.g., phytate, citrate, or malonate) to the hydrogen peroxide. When the hydrogen peroxide–organic acid mixture is injected into the subsurface, the labile transition metals in the subsurface would bind to the organic acid, reducing their catalytic activity and lowering the rate of hydrogen peroxide decomposition.

1.2.3 Hydrogen Peroxide Decomposition and Stabilization in Subsurface Solids

Hydrogen peroxide stabilization was evaluated in four characterized subsurface solids from Georgia, Maine, California, and Washington State. The depth of collection and subsurface solid characteristics are listed in Table 1-2. (The subsurface solids used for treatability studies should be collected from the same depth that injections will take place.) Site-specific stratigraphic data from samples collected for CHP treatability studies should be used to support CHP decision-making. The U.S. Department of Agriculture (USDA)/Natural Resource Conservation Service (NRCS) Soil Survey database can be used to provide site-specific physical and chemical soil data. Site data can be accessed via the website:

http://cp.mcafee.com/d/avndzgOcy0Orhpd7bbVEV7fTvdTdzDSnQSm3oVZBZdBYSDtBxBxV4sUrjKOy-YUyYyrlrwh-8a9Aj-ndAO9_bCXImd7dQmn-LP1EVp7ecZuVtddxPD3hOyUZvBHFShhlLt_BgYF6lK1FJ4SCrKrKr01w2FmhZ6UCvbtiT

uhGpVKy6YhGpMgmmMbRlYbqh_w26RECq78EFCzB1AsgpvezaNfoEtI4fziIevv1jteRTB
p7CS7QT3ob6Azh1iIzPh1o_qkAXaSPBm53qr1I7OVMD15)

Hydrogen peroxide decomposition in aqueous hydrogen peroxide slurries containing the Georgia subsurface solid is shown in Figure 1-2a–b. The hydrogen peroxide half-life in this slurry was approximately 4 hr. Phytate addition at both 10 mM and 250 mM increased the hydrogen peroxide half-life; with 10 mM phytate addition, the hydrogen peroxide half-life increased to 9 hr (Figure 1-2a), and the addition of 250 mM increased the half-life to 15 hr (Figure 1-2b). Malonate and citrate were also effective in increasing the hydrogen peroxide half-life; 10 mM malonate or citrate increased the half-life to 6 hr, and 1 M citrate or malonate increased the half-life to 7 hr.

Table 1-2. Characteristics of the Georgia, Maine, California and Washington subsurface solids.

	Subsurface Solids			
	Georgia	**Maine**	**California**	**Washington**
Sand (%)	47.4	54.0	78.7	32.4
Silt (%)	14.3	33.5	8.0	15.6
Clay (%)	38.3	12.5	13.3	52.0
USDA soil texture class	Sandy clay	Sandy clay loam	Sandy loam	Clay
Depth of collection (m)	6–8	4–5	2–3	< 1
Crystalline iron oxides (mg/kg)	4,300	7,200	11,000	6,900
Crystalline manganese oxides (mg/kg)	170	183	340	380
Amorphous iron oxides (mg/kg)	16	8	780	150
Amorphous manganese oxides (mg/kg)	160	250	330	360
Organic carbon (%)	0.062	0.51	0.08	1.08
Surface area (m^2/g)	5.5	2.5	1.5	6.3
Cation exchange capacity (cmol/kg)	7.9	3.6	22.0	25.0

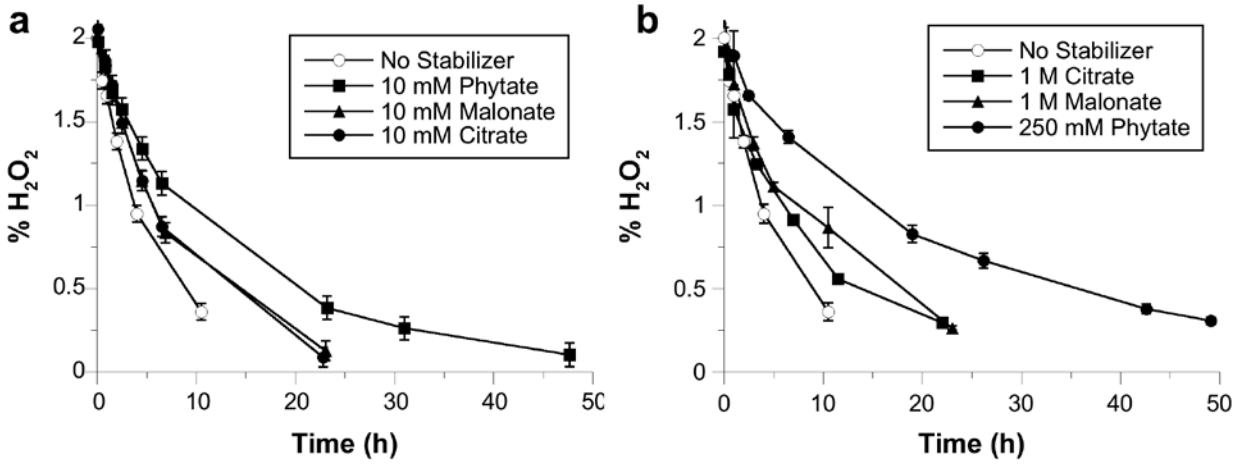


Figure 1-2. Decomposition of hydrogen peroxide in the Georgia subsurface solid without stabilization or with addition of citrate, malonate, or phytate. (a) 10 mM stabilizer; (b) 1 M or 250 mM stabilizer

Hydrogen peroxide decomposition in the presence of the Maine subsurface solid under unstabilized conditions and stabilized by two concentrations of the stabilizers phytate, citrate, and malonate is shown in Figure 1-3a–b. Under conditions of no stabilization, the hydrogen peroxide half-life was 1.5 hr. Stabilization of the Maine subsurface solid with phytate was highly effective; 10 mM phytate addition increased the hydrogen peroxide half-life to 10 hr, and 250 mM phytate addition increased the half-life to 32 hr. As with the Georgia subsurface solid, the effectiveness of malonate and citrate stabilizers was similar. Addition of 10 mM citrate or 10 mM malonate increased the hydrogen peroxide half-life to 4 hr. Using 1 M citrate or malonate, the hydrogen peroxide half-life increased to 5 hr for citrate and 8 hr for malonate.

Hydrogen peroxide decomposition without stabilization in the California subsurface solid slurry was rapid with a half-life of <0.5 hr (Figure 1-4a–b). However, stabilization with phytate was highly effective, increasing the half-life to 12 hr with 10 mM phytate addition and 26 hr with 250 mM phytate addition. Stabilization using citrate and malonate was strongly influenced by the

stabilizer concentration. Using 10 mM citrate or malonate, the hydrogen peroxide half-life increased to 2 hr; however, when 1 M citrate was added to the slurries the hydrogen peroxide half-life increased to 6 hr, and when 1 M malonate was added, the half-life increased to 12 hr.

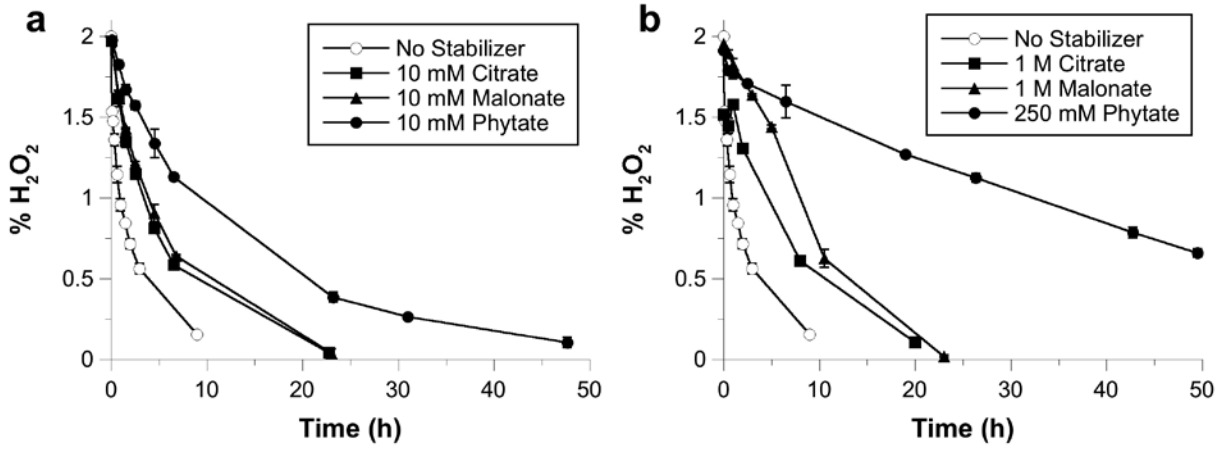


Figure 1-3. Decomposition of hydrogen peroxide in the Maine subsurface solid without stabilization or with addition of citrate, malonate, or phytate. (a) 10 mM stabilizer; (b) 1 M or 250 mM stabilizer

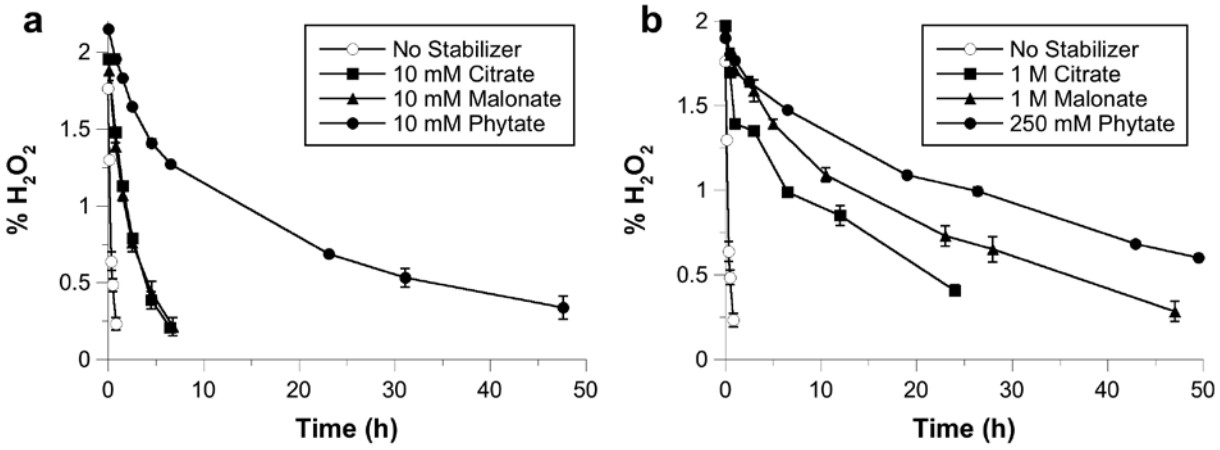


Figure 1-4. Decomposition of hydrogen peroxide in the California subsurface solid without stabilization or with addition of citrate, malonate, or phytate. (a) 10 mM stabilizer; (b) 1 M or 250 mM stabilizer

Hydrogen peroxide concentrations as a function of time in slurries containing the Washington subsurface solid with and without stabilization are shown in Figure 1-5a–b. The unstabilized hydrogen peroxide half-life in the Washington subsurface solid was 4 hr. Hydrogen peroxide decomposition in the Washington subsurface solid was unique among the four solids studied in that all three stabilizers were equally effective, and the stabilizer concentration had minimal effect on the rate of hydrogen peroxide decomposition. The hydrogen peroxide half-life for all three stabilizers at 10 mM concentrations was approximately 12 hr and at high (250 mM or 1 M) stabilizer concentrations was 18–22 hr.

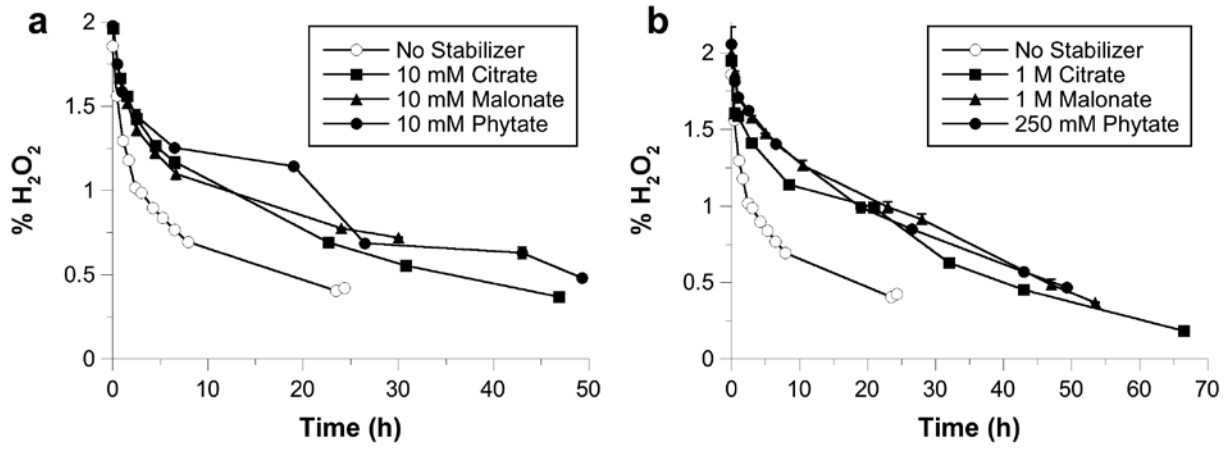


Figure 1-5. Decomposition of hydrogen peroxide in the Washington subsurface solid without stabilization or with addition of citrate, malonate, or phytate. (a) 10 mM stabilizer; (b) 1 M or 250 mM stabilizer

The results shown in Figures 1-2 through 1-5 demonstrate that stabilization of hydrogen peroxide was most effective with phytate in the three subsurface solids from Georgia, Maine, and California, while citrate, malonate, and phytate were equally effective in stabilizing hydrogen

peroxide in the subsurface solid collected from Washington state. The two characteristics of the Washington solid that are notably different from the other solids are the clay content and the soil organic carbon (SOC) content. Both clays and SOC exchange metals, such as iron and manganese, and these exchanged forms of transition metals have been shown to be active as CHP catalysts (Huling et al., 2001; Hui, 2001). Citrate, malonate, and phytate may be equally incapable of deactivating these exchanged transition metals, which would result in lesser, and near-equal, degrees of stabilization for the three ligands.

1.2.4 Effect of Stabilizers on Hydroxyl Radical Generation

Increased hydrogen peroxide stability beyond what is currently observed in the field is critical to the effective implementation of CHP ISCO; however, the activity of the reactive oxygen species generated in the CHP systems must be maintained when the hydrogen peroxide is stabilized. Therefore, the relative rates of oxidant and reductant generation were evaluated in stabilized and unstabilized hydrogen peroxide slurries containing the Georgia, Maine, California, and Washington solids. The relative production of hydroxyl radical in slurries of each of the four solids with and without stabilization by 10 mM phytate was measured by oxidation of the probe molecule hexanol (Figure 1-6a–d). Relative rates of hydroxyl radical generation in the unstabilized systems were different for each of the four subsurface solids. Relative hydroxyl radical production in the Georgia subsurface solid was greater without phytate than with phytate, with only 10% of the hexanol oxidized with phytate addition and 36% oxidized without phytate addition relative to the control (Figure 1-6a). There was minimal difference in relative hydroxyl radical generation between the unstabilized and stabilized slurries of the Maine subsurface solid and the California subsurface solid, with 68% and 80% oxidation of the hexanol in the stabilized and unstabilized Maine subsurface solid, respectively, and 90% and 81% oxidation in the

stabilized and unstabilized California subsurface solid, respectively (Figures 1-6b and 1-6c). The relative rate of hydroxyl radical production was low in the Washington subsurface solid, and there was little difference in hexanol oxidation rates between the systems with and without phytate addition, with 15% and 11% oxidation of the hexanol in the stabilized and unstabilized systems (Figure 1-6d).

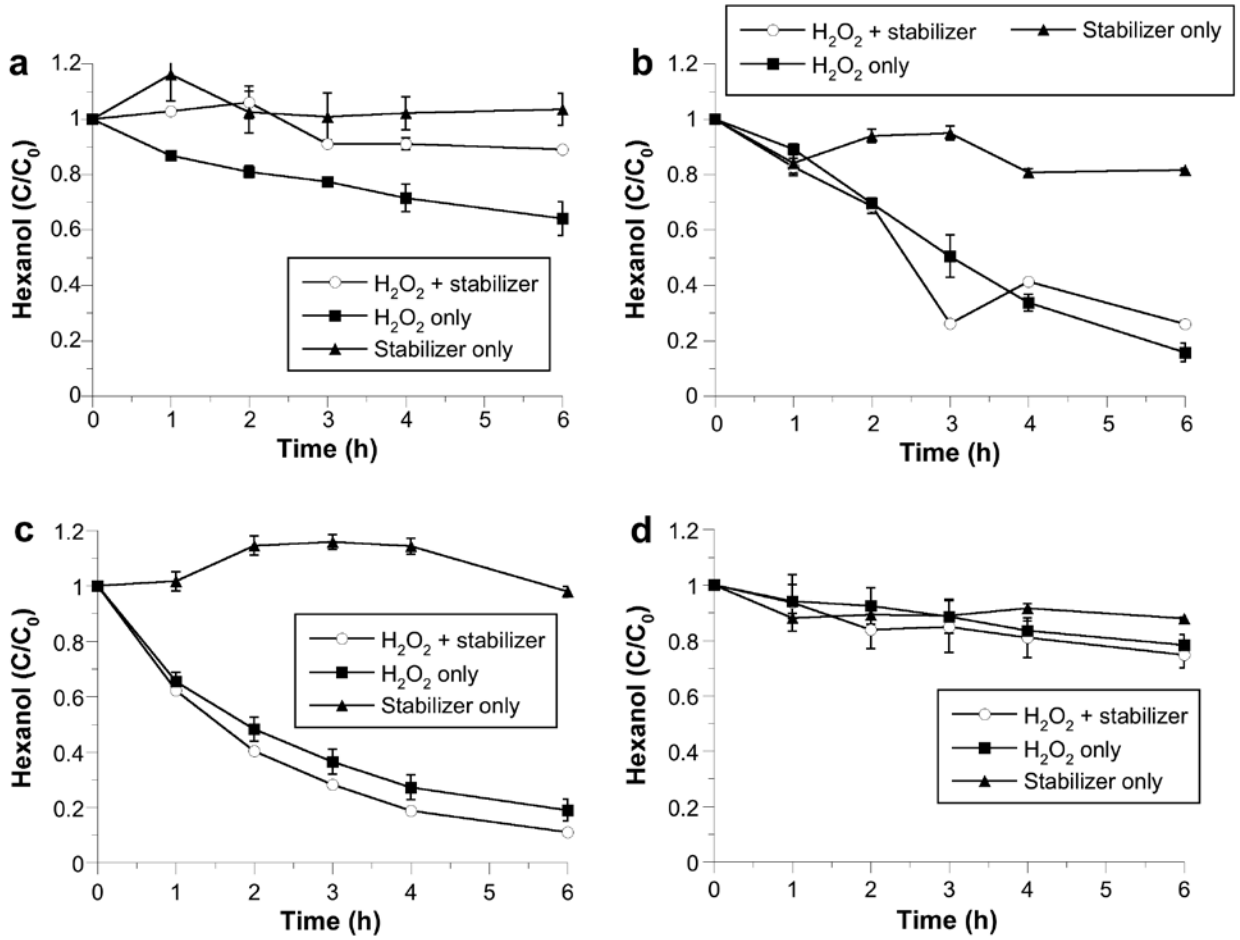


Figure 1-6. Relative activity of hydroxyl radical measured by hexanol oxidation in four subsurface solids with and without stabilization with 10 mM phytate. (a) Georgia subsurface solid; (b) Maine subsurface solid; (c) California subsurface solid; (d) Washington subsurface solid

Relative rates of hydroxyl radical generation in CHP slurries containing each of the four solids with and without citrate stabilization are shown in Figures 1-7a–d. In Georgia subsurface solid slurries, a higher rate of hydroxyl radical generation was found without citrate addition than with citrate stabilization; nonetheless, oxidation of the hydroxyl radical probe was slow in both, with 30% hexanol oxidation in the unstabilized systems and 8% oxidation in the citrate-stabilized systems relative to the control (Figure 1-7a). There was minimal difference in hydroxyl radical activity between the unstabilized and citrate-stabilized systems in slurries of the Maine subsurface solid, with 77% hexanol oxidation in the stabilized system and 70% in the unstabilized system (Figure 1-7b). However, relative hydroxyl radical production in the California subsurface solid (Figure 1-7c) was markedly different. Relative hydroxyl radical production was significantly greater with citrate stabilization, with 84% hexanol oxidation in the citrate-stabilized system, and 28% oxidation in the unstabilized system. Similar results were observed in the CHP systems with the Washington subsurface solid (Figure 1-7d); 32% hexanol oxidation occurred with citrate stabilization, while 14% hexanol oxidation was observed in the stabilized systems.

The relative rates of hydroxyl radical generation in solid slurries with and without malonate stabilization are shown in Figure 1-8a–d. These data indicate that the presence of malonate has a significant effect on hydroxyl radical generation rates in some solid systems but not in others. Rates of hydroxyl radical generation in the unstabilized and malonate-stabilized Georgia subsurface solid were not significantly different, with approximately 43% of the hydroxyl radical probe hexanol oxidized in each relative to control systems (Figure 1-8a). In the Maine subsurface solid, however, hydroxyl radical generation rates were greater in the stabilized system, with >99% of the hydroxyl radical probe oxidized in the system with malonate,

compared to 80% hexanol oxidation in the unstabilized system (Figure 1-8b). Relative hydroxyl radical generation rates were also greater with malonate stabilization in the California subsurface solid at >99%, compared to 44% in unstabilized systems (Figure 1-8c). A similar trend was observed in the Washington subsurface solid; the relative hydroxyl radical generation rate in the malonate-stabilized systems was 52% compared to 35% in the unstabilized systems (Figure 1-8d).

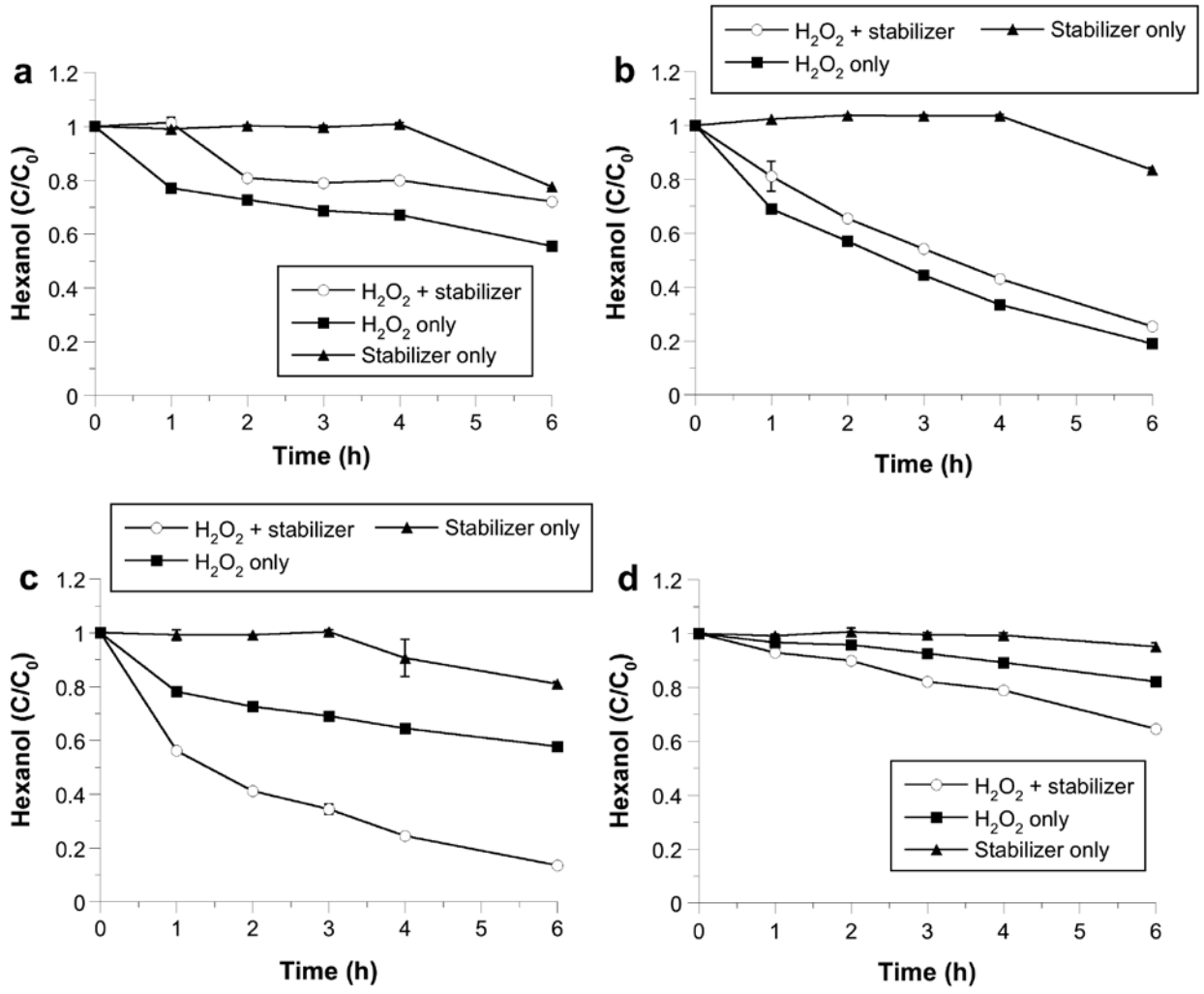


Figure 1-7. Relative activity of hydroxyl radical measured by hexanol oxidation in four subsurface solids with and without stabilization with 10 mM phytate. (a) Georgia subsurface solid; (b) Maine subsurface solid; (c) California subsurface solid; (d) Washington subsurface solid

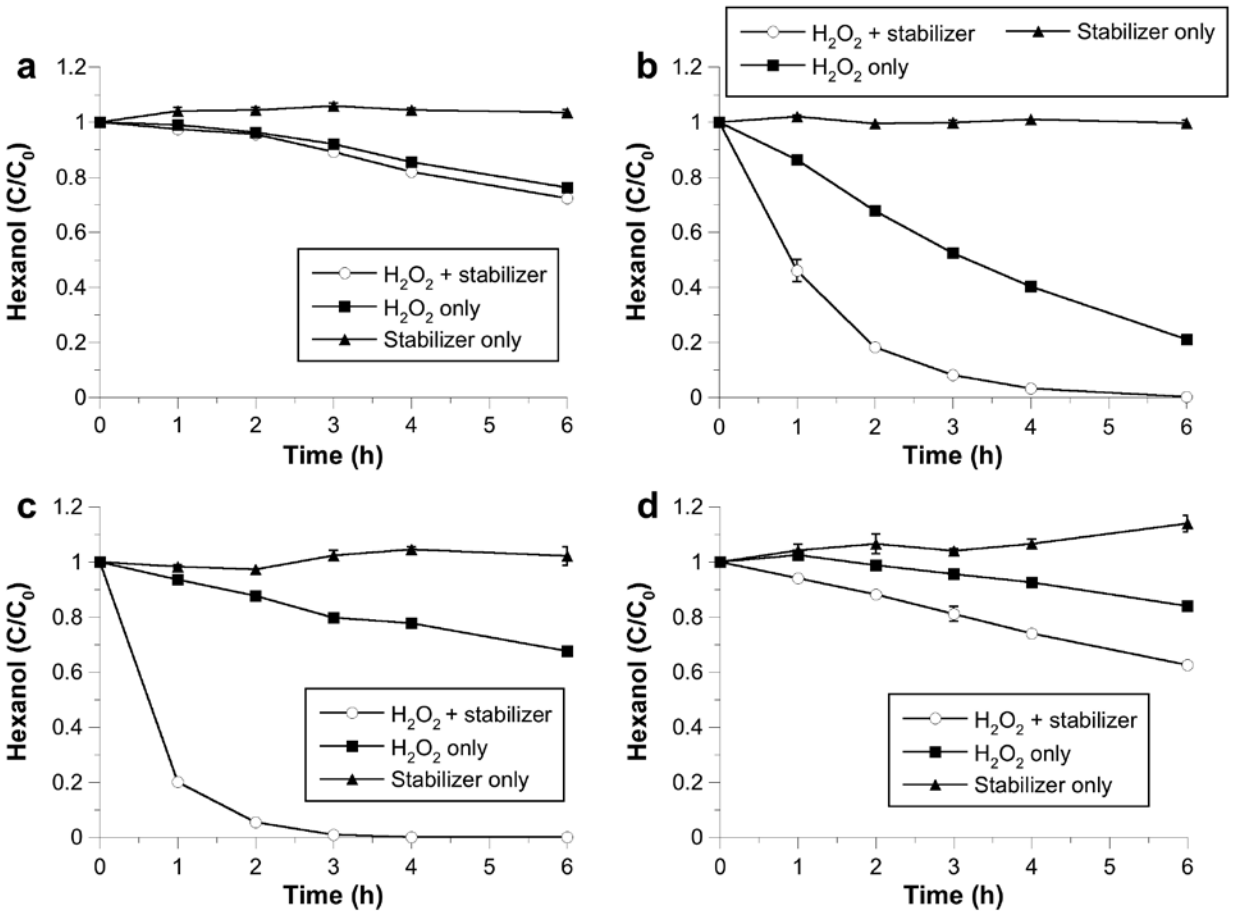


Figure 1-8. Relative activity of hydroxyl radical measured by hexanol oxidation in four subsurface solids with and without stabilization with 10 mM malonate. (a) Georgia subsurface solid; (b) Maine subsurface solid; (c) California subsurface solid; (d) Washington subsurface solid

Based on the data shown in Figures 1-6 through 1-8, the systems that showed increased relative hydroxyl radical generation in stabilized systems apparently did so because the oxidant source, hydrogen peroxide, was maintained in the slurries. The highest increase in stabilization occurred in the California subsurface solid system, and hydroxyl radical generation increased in this system with each of the stabilizers. Baciocchi et al. (2004) documented that the residual hydrogen peroxide concentration is as important parameter in CHP contaminant oxidation. The results shown in Figures 1-4a and 1-6c, 1-7c, and 1-8c strongly suggest the maintenance of the

hydrogen peroxide residual aids in maintaining hydroxyl radical generation in the California subsurface solid system.

For each of the four solids systems, addition of phytate had the most negative overall effect on the relative rates of hydroxyl radical generation; it had minimal effect on hydroxyl radical generation rates in the California and Washington solids systems, and decreased hydroxyl radical generation rates in the Georgia and Maine solids systems. In contrast, the addition of malonate had the most positive overall effect on relative hydroxyl radical generation rates in each of the four solids systems; it had minimal effect on hydroxyl radical generation rates in the Georgia solid slurries (compared to the decrease seen with phytate and malonate), and increased hydroxyl radical generation rates is the other three systems. The positive effect of malonate on hydroxyl radical activity is likely related to it slow rate of reactivity with hydroxyl radicals (k_{OH}. $= 2.0 \times 10^7\ M^{-1}\ sec^{-1}$).

1.2.5 Effect of Stabilizers on Superoxide Generation

The effect of phytate stabilization on superoxide generation in the four solids systems using the probe molecule hexachloroethane (HCA) is shown in Figures 1-9a–d. The relative rates of superoxide generation were greater in all four of the unstabilized systems relative to the phytate-stabilized systems. The difference in relative superoxide generation was small in the Georgia subsurface solid slurries with 78% HCA degradation without phytate addition and 64% HCA degradation in the phytate-stabilized system relative to the control (Figure 1-9a). Differences in relative superoxide generation were more pronounced in CHP reactions conducted in slurries of the Maine subsurface solid (Figure 1-9b). Under conditions of no stabilization, 73% of the HCA was degraded, while 40% of the HCA was degraded in the phytate-stabilized systems. The differences in superoxide generation were even more pronounced in the California

subsurface solid system, with 70% of the HCA degraded in the unstabilized system and 22% of the HCA degraded in the phytate-stabilized systems (Figure 1-9c). A difference similar to that of the Georgia subsurface solids system was observed with CHP reactions in the Washington subsurface solid, with 63% HCA degradation in unstabilized system and 53% HCA degradation in the presence of phytate (Figure 1-9d).

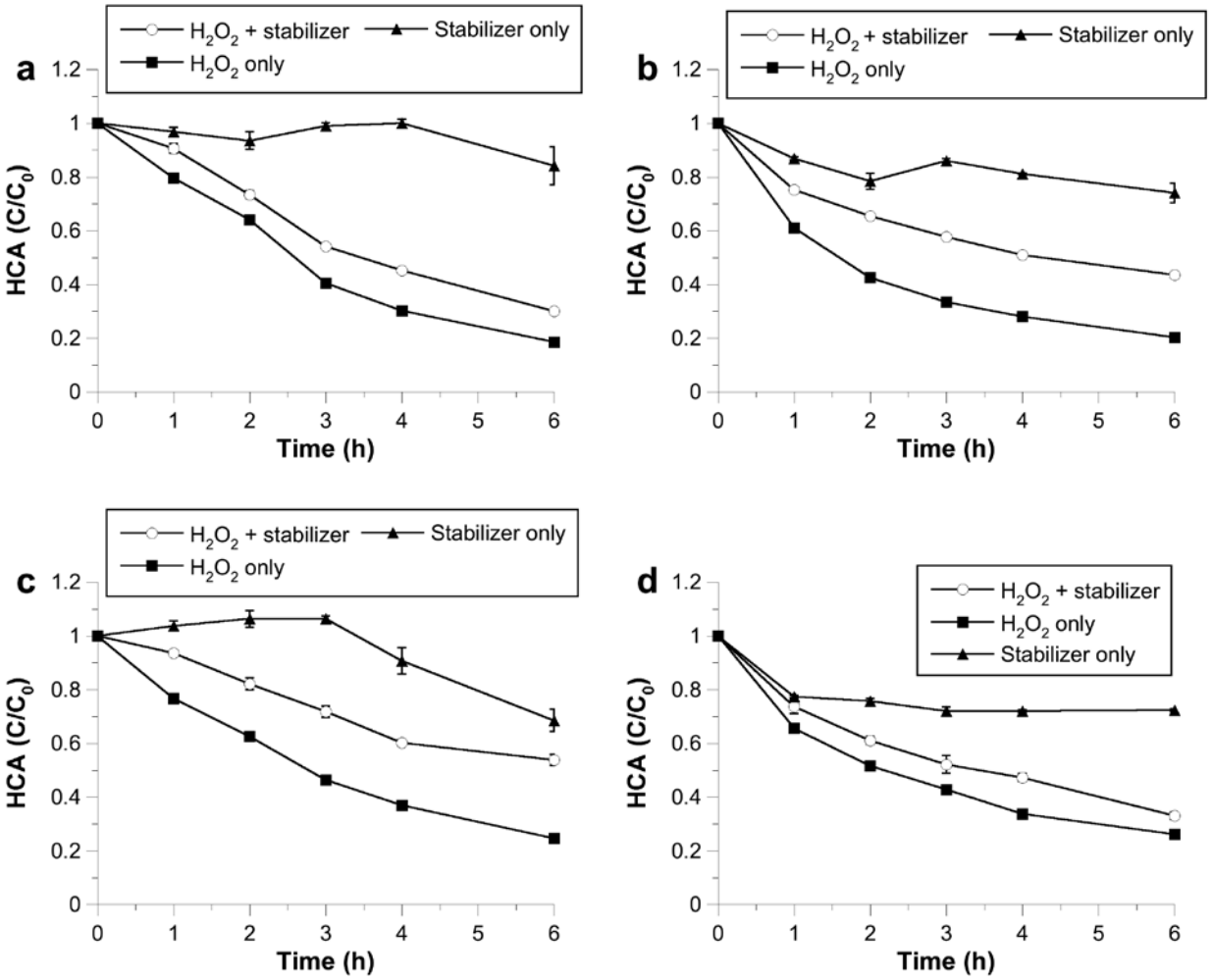


Figure 1-9. Relative activity of superoxide measured by hexachloroethane (HCA) destruction in four subsurface solids with and without stabilization with 10 mM phytate. (a) Georgia subsurface solid; (b) Maine subsurface solid; (c) California subsurface solid; (d) Washington subsurface solid

Relative rates of superoxide generation in unstabilized and citrate-stabilized subsurface solids during CHP reactions are shown in Figures 1-10a–d. Small differences in relative rates of superoxide generation were observed in CHP reactions in the four solids slurries. There was a small difference in relative rates of superoxide generation between unstabilized and citrate-stabilized samples of the Georgia subsurface solid, with 73% HCA degradation the unstabilized system and 60% HCA degradation in the presence of citrate (Figure 1-10a). Similarly, in Maine subsurface solid slurries, unstabilized hydrogen peroxide provided slightly higher rates of superoxide generation (Figure 1-10b), with 54% and 45% HCA degradation in the unstabilized and stabilized systems, respectively. Differences in relative superoxide generation were minimal in slurries of the California subsurface solid (Figure 1-10c) with 75% and 83% HCA degradation in the unstabilized and stabilized systems, and in the Washington subsurface solid (Figure 1-10d), with 59% HCA degradation in the unstabilized system and 63% HCA degradation in the stabilized system.

Relative rates of superoxide generation for unstabilized and malonate-stabilized CHP reactions in the four solids are shown in Figures 1-11a–d. As with the other stabilizers, HCA degradation was generally lower in the stabilized systems, although the differences between unstabilized and stabilized systems were generally small. Addition of malonate decreased relative superoxide generation rates in Georgia subsurface solid slurries, with 95% and 78% HCA degradation in the unstabilized and stabilized systems, respectively (Figure 1-11a). The greatest difference in relative superoxide generation was in the Maine subsurface solids, with 80% HCA degradation in unstabilized subsurface solid slurries compared to 52% HCA degradation in slurries stabilized with malonate (Figure 1-11b). Differences in relative superoxide generation rates between unstabilized and malonate-stabilized systems were minimal

in slurries of the California subsurface solid and the Washington subsurface solid (Figures 1-11c–d). HCA degradation in unstabilized and stabilized systems was 78% and 73% for the California subsurface solid. In the Washington subsurface solid, the HCA degradation was 59% in the unstabilized system and 64% in the stabilized system.

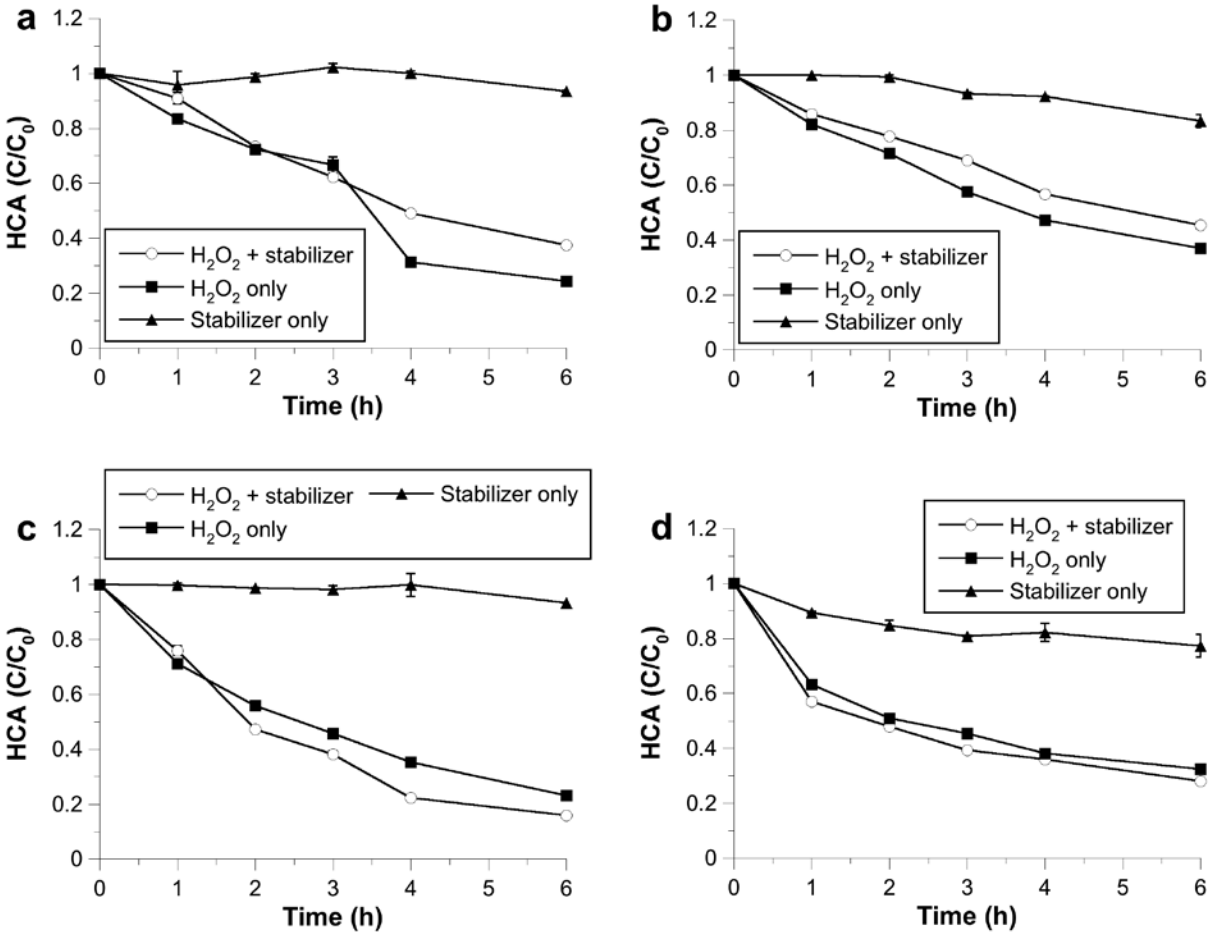


Figure 1-10. Relative activity of superoxide measured by hexachloroethane (HCA) destruction in four subsurface solids with and without stabilization with 10 mM citrate. (a) Georgia subsurface solid; (b) Maine subsurface solid; (c) California subsurface solid; (d) Washington subsurface solid

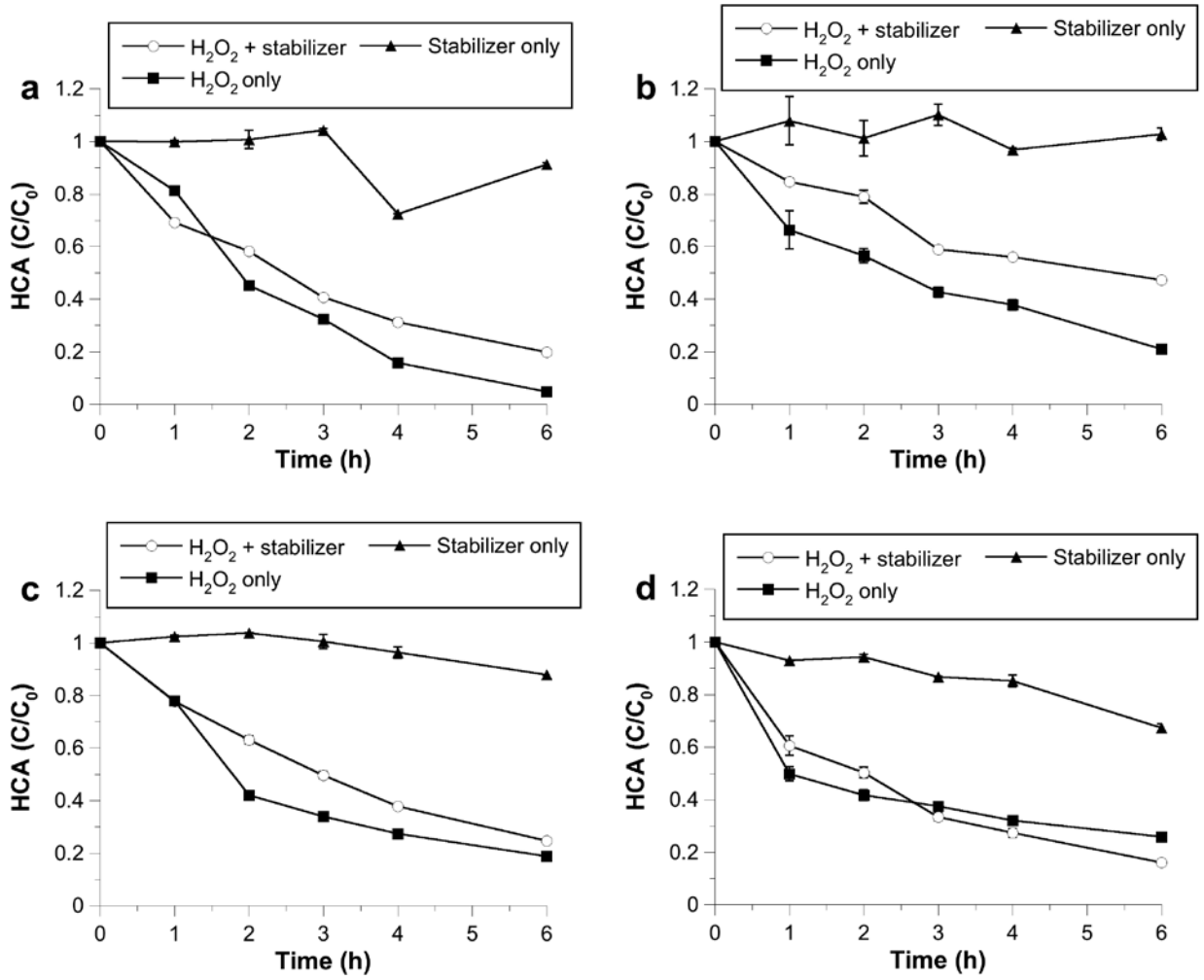


Figure 1-11. Relative activity of superoxide measured by hexachloroethane (HCA) destruction in four subsurface solids with and without stabilization with 10 mM malonate. (a) Georgia subsurface solid; (b) Maine subsurface solid; (c) California subsurface solid; (d) Washington subsurface solid

The results of Figures 1-9 through 1-11 demonstrate that superoxide was generated in all four solids systems. The relative rates of superoxide generation were usually somewhat lower in the stabilized systems relative to the unstabilized systems, but there was no consistent trend between stabilizers or between solids. The data suggest that in some systems, the stabilizer may

scavenge superoxide. However, relative rates of superoxide generation in stabilized systems do not appear to be lowered sufficiently to negatively affect CHP remediation.

The results shown in Figures 1-6 through 1-11 of relative rates of hydroxyl radical generation and relative rates of superoxide generation in unstabilized and stabilized hydrogen peroxide–solid slurries demonstrate that stabilization usually had a minimal negative effect on the generation of these reactive oxygen species. Relative hydroxyl radical generation rates increased in some stabilized systems and decreased in other stabilized systems relative to the corresponding rates in unstabilized systems; however, most of the differences between the relative rates of generation were minimal and should not negatively impact the efficacy of CHP treatment. Relative rates of superoxide generation were usually lower in the stabilized systems. Nonetheless, relative rates of hydroxyl radical generation and superoxide generation in CHP systems were not significantly affected by stabilization.

1.2.6 CHP Stabilization in One-Dimensional Columns

One-dimensional saturated columns of iron-coated sand (ICS) and manganese-coated sand (MCS) were also used to investigate the effectiveness of the stabilizers in slowing hydrogen peroxide decomposition during its transport through a model subsurface system. Phytate was used as a stabilizer in ICS columns and both phytate and citrate were used as stabilizers in MCS columns. The concentrations of unstabilized hydrogen peroxide in each of the eight ports of the ICS column over 100 min and 4000 mL of cumulative flow are shown in Figure 1-12. Hydrogen peroxide residuals were detected in Port 1 throughout the first 3250 mL of flow, but hydrogen peroxide concentrations were dramatically lower in Ports 2 and 3, with no detectable hydrogen peroxide reaching Port 4 and beyond. These results are similar to hydrogen peroxide decomposition rates found in subsurface systems containing high concentrations of iron or

manganese oxides, which result in hydrogen peroxide half-lives of < 30 min (Watts and Teel, 2005). Hydrogen peroxide concentrations at different column depths over 150 min and 6600 mL in a parallel system with the addition of 25 mM phytate are shown in Figure 1-13. Higher hydrogen peroxide residuals were detected in Port 1 (4.4%) compared to unstabilized hydrogen peroxide. Furthermore, in contrast to Figure 1-12, significant residuals were detected in all of the lower ports in succession, including a maximum hydrogen peroxide concentration of 3.3% at Port 8.

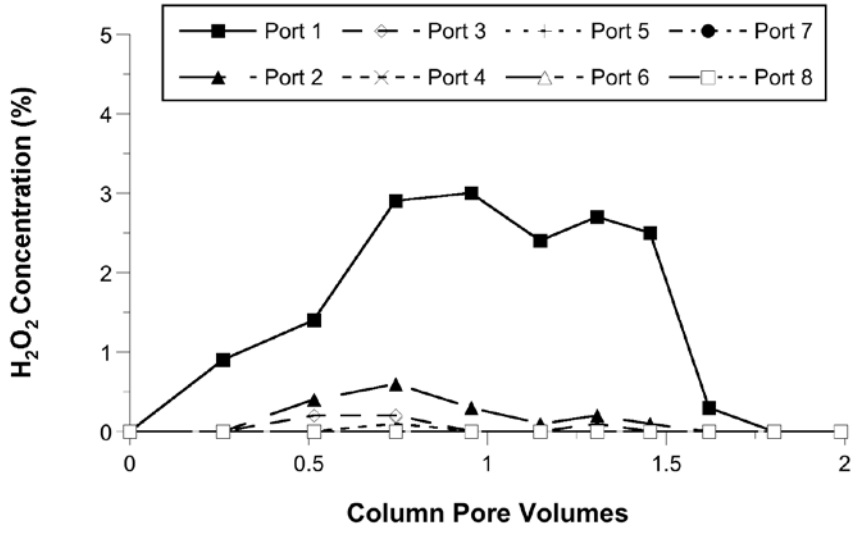


Figure 1-12. Concentration of unstabilized 5% H_2O_2 at eight ports in a column of iron-coated sand

The total mass of hydrogen peroxide passing through the column at each port in the unstabilized and stabilized ICS columns was calculated by integrating the area under each line (Figure 1-14). The total mass of hydrogen peroxide passing through the unstabilized column was 61 g at Port 1 and decreased to 0.2 g at Port 4, with undetectable masses at Ports 5–8. In contrast, the total mass of hydrogen peroxide passing through the phytate-stabilized column at Port 1 was 154 g, decreasing to 36 g at Port 8. The results of Figures 1-12 through 1-14 show a significant

increase in hydrogen peroxide lifetime relative to the unstabilized hydrogen peroxide. These results demonstrate that phytate is effective in stabilizing hydrogen peroxide as it is transported through an ICS matrix.

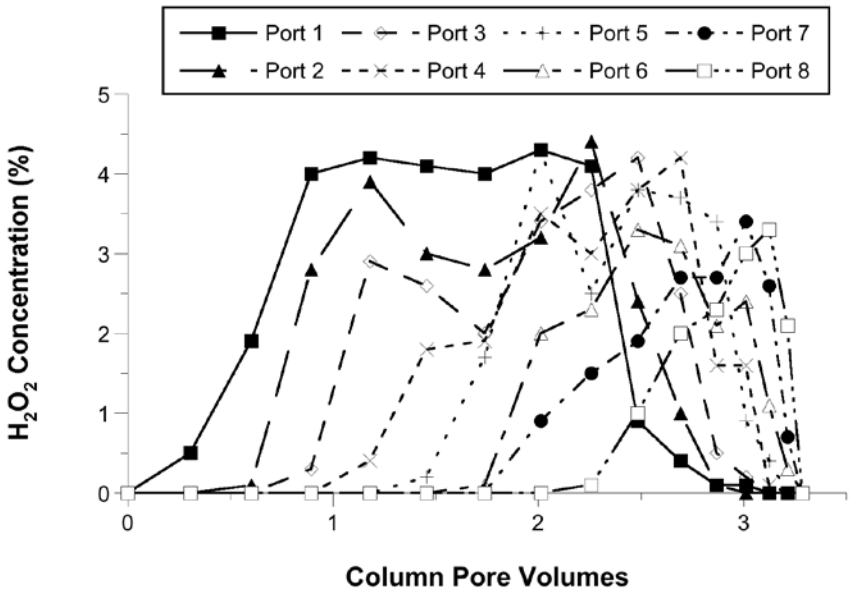


Figure 1-13. Concentration of 5% H_2O_2 stabilized by 25 mM phytate at eight ports in a column of iron-coated sand

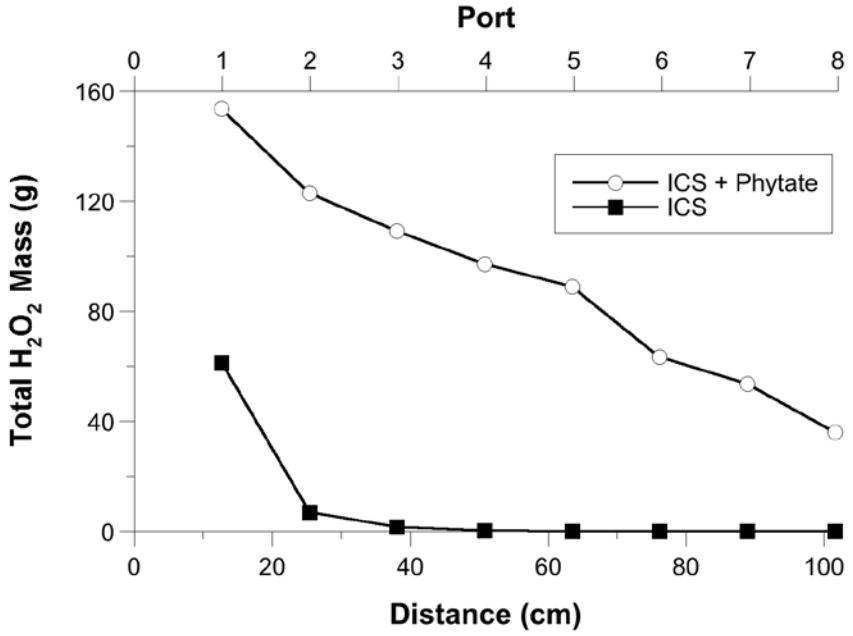


Figure 1-14. Total hydrogen peroxide mass at each of eight ports in iron-coated sand columns with and without 25 mM phytate

The concentrations of unstabilized hydrogen peroxide in each of the eight ports of the MCS column over 140 min and 4000 mL of cumulative flow are shown in Figure 1-15. The concentrations of hydrogen peroxide along the phytate-stabilized and citrate-stabilized columns are shown in Figures 1-16 and 1-17, respectively. The maximum hydrogen peroxide concentration at Port 1 in the unstabilized column was 4.8% (Figure 1-15); the hydrogen peroxide concentration decreased slightly at each of the ports to a maximum concentration of 3.8% in Port 8. In the column stabilized with 25 mM phytate (Figure 1-16), the maximum hydrogen peroxide concentration at each of the eight ports remained at 4.7–5%. In the MCS column stabilized with 25 mM citrate (Figure 1-17), the maximum hydrogen peroxide concentration observed at each port decreased from 4.8% at Port 1 to 4.4% at Port 8.

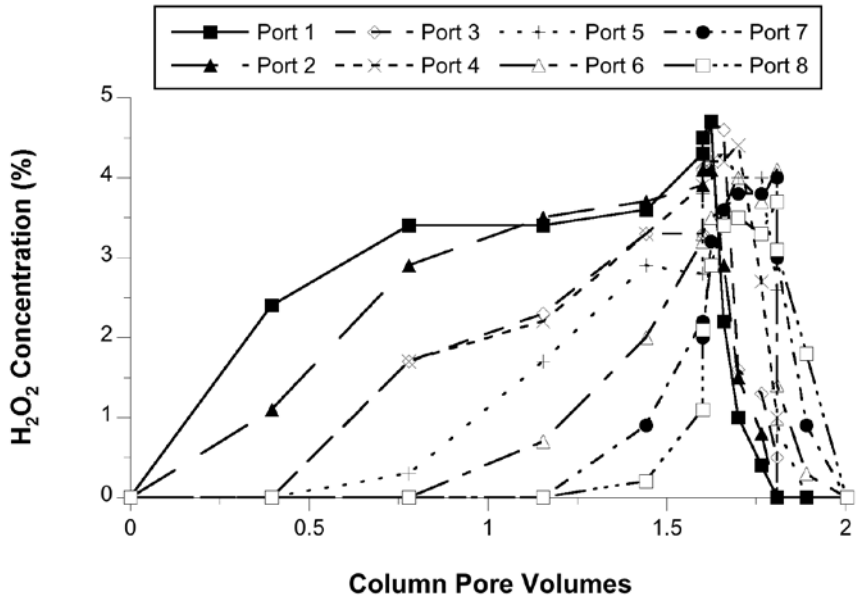


Figure 1-15. Concentration of unstabilized 5% H_2O_2 at eight ports in a column of manganese-coated sand

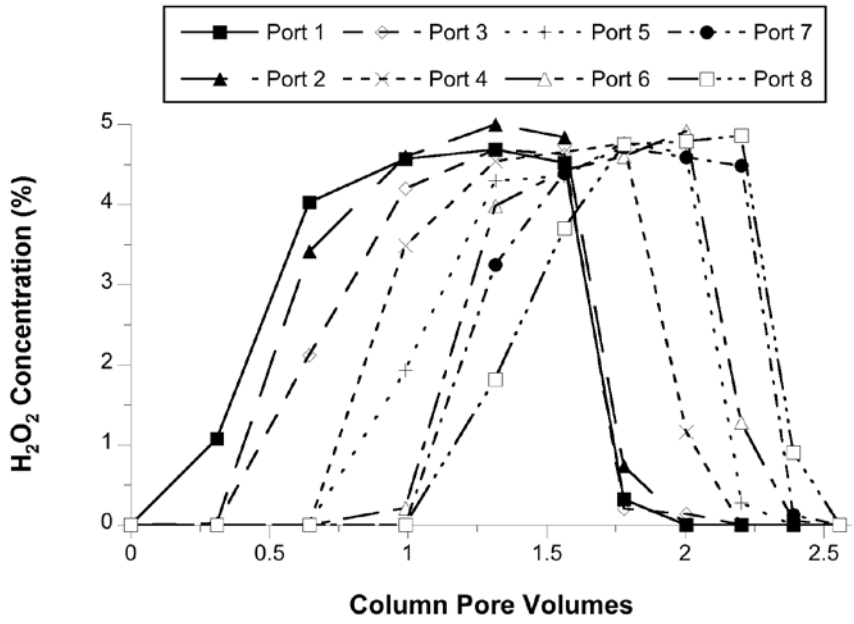


Figure 1-16. Concentration of 5% H_2O_2 stabilized by 25 mM phytate at eight ports in a column of manganese-coated sand

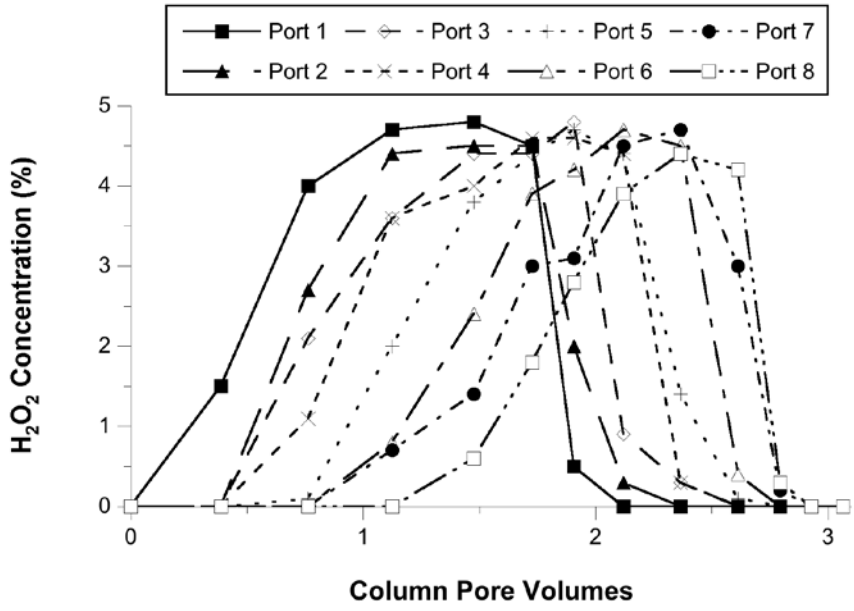


Figure 1-17. Concentration of 5% H_2O_2 stabilized by 25 mM citrate at eight ports in a column of manganese-coated sand

The total mass of hydrogen peroxide passing through the column at each port for unstabilized, phytate-stabilized, and citrate-stabilized MCS columns is shown in Figure 1-18. The total masses for the phytate-stabilized and citrate-stabilized MCS columns were significantly greater than those in the unstabilized MCS column. In the unstabilized column, the total mass of hydrogen peroxide ranged from 97 g at Port 1 to 20 g at Port 8. In contrast, the total mass ranged from 114 g at Port 1 to 89 g at Port 8 in the phytate-stabilized column, and from 124 g at Port 1 to 81 g at Port 8 in the citrate-stabilized column. These results suggest that citrate and phytate are equally effective in stabilizing manganese oxide-mediated hydrogen peroxide decomposition.

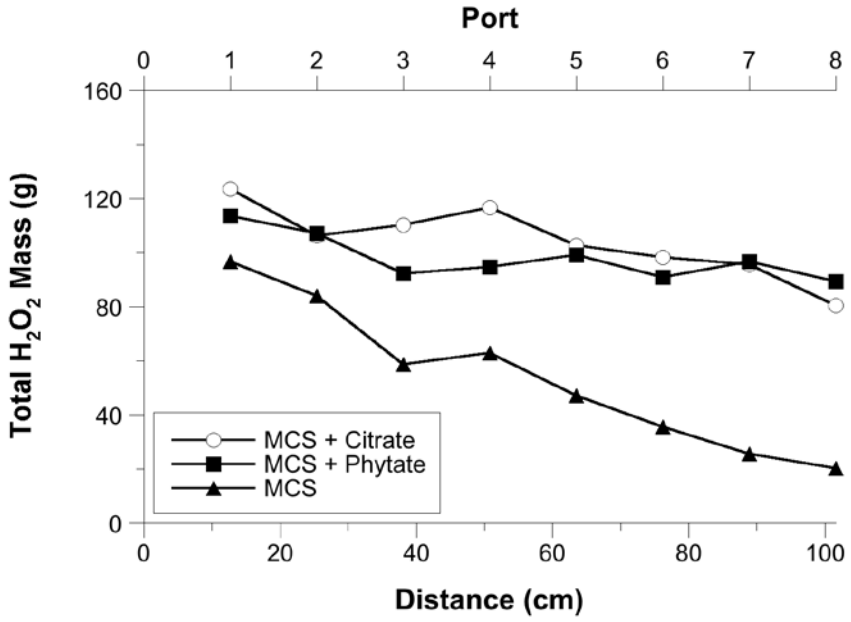


Figure 1-18. Total hydrogen peroxide mass measured at each of eight ports in manganese-coated sand columns with and without 25 mM phytate or citrate

1.2.7 Stabilizer Transport in One-Dimensional Columns

An important aspect of hydrogen peroxide stabilization is the transport dynamics of the stabilizer after injection into the subsurface. The concentration of phytate in each port of the ICS column over 130 min and 3250 mL of cumulative flow is shown in Figure 1-19. Phytate concentrations of 20–25 mM were observed sequentially in each port, demonstrating that phytate was not degraded in the column. In addition, transport of phytate through the column was not retarded relative to the rate of hydrogen peroxide transport (Figure 1-13). The concentrations of citrate and phytate in each port of the MCS column as a function of cumulative flow are shown in Figures 1-20 and 1-21, respectively. Similar to results in the ICS system, the stabilizers were not retarded in the column and did not degrade. The masses of stabilizers passing through the columns at each port are shown in Figure 1-22; no significant changes in mass of phytate or citrate were found. These results are expected; the second order reaction rate of hydroxyl radical with citrate is 5×10^7 M^{-1} sec^{-1} (Buxton et al., 1988), which is essentially unreactive with hydroxyl radical because scavenging reactions occur at the approximately the same rate (Watts and Teel, 2005). Although the reactivity of hydroxyl radical with phytate (inositol hexaphosphate) has not been reported, it is likely similar to the slow rate of hydroxyl radical reaction with the structurally similar compound inositol hexasulfate, which is 1×10^7 M^{-1} sec^{-1} (Buxton et al., 1988). The results of Figures 1-20–1-22 confirm that these two stabilizers are not destroyed by the reactive oxygen species generated in CHP reactions, and therefore have the potential to stabilize hydrogen peroxide throughout the radius of influence during injections into the subsurface.

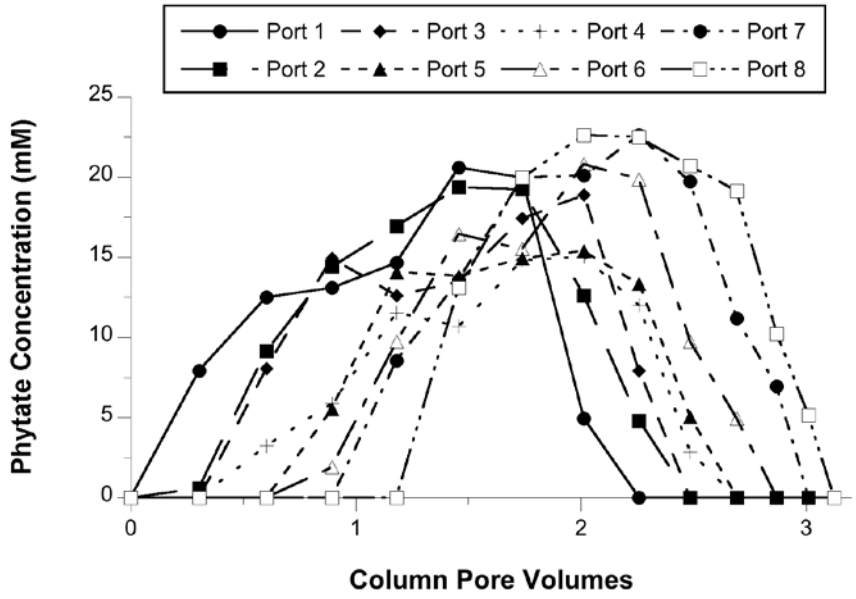


Figure 1-19. Concentration of phytate in each of eight ports compared to cumulative flow in a column of iron-coated sand treated with 5% H_2O_2 stabilized by 25 mM phytate

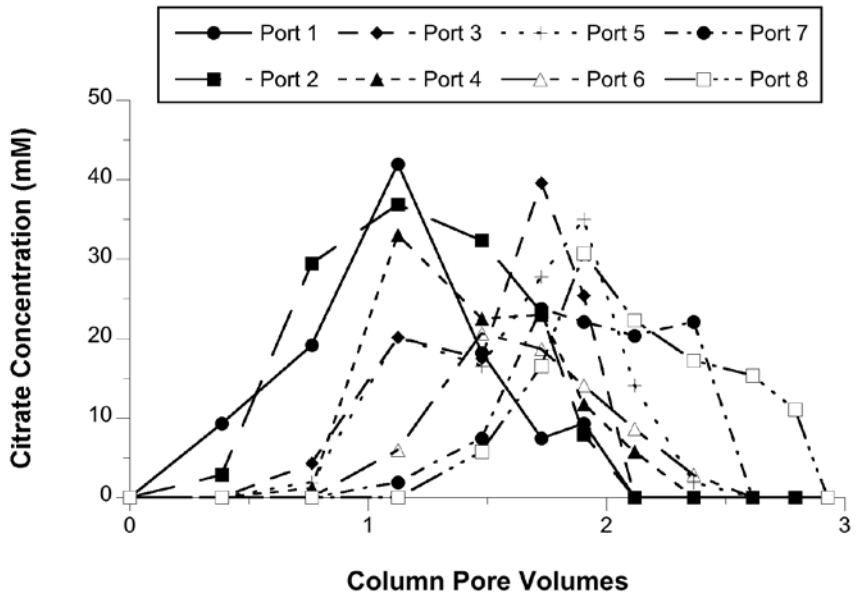


Figure 1-20. Concentration of citrate in each of eight ports compared to cumulative flow in a column of manganese-coated sand treated with 5% H_2O_2 stabilized by 25 mM citrate

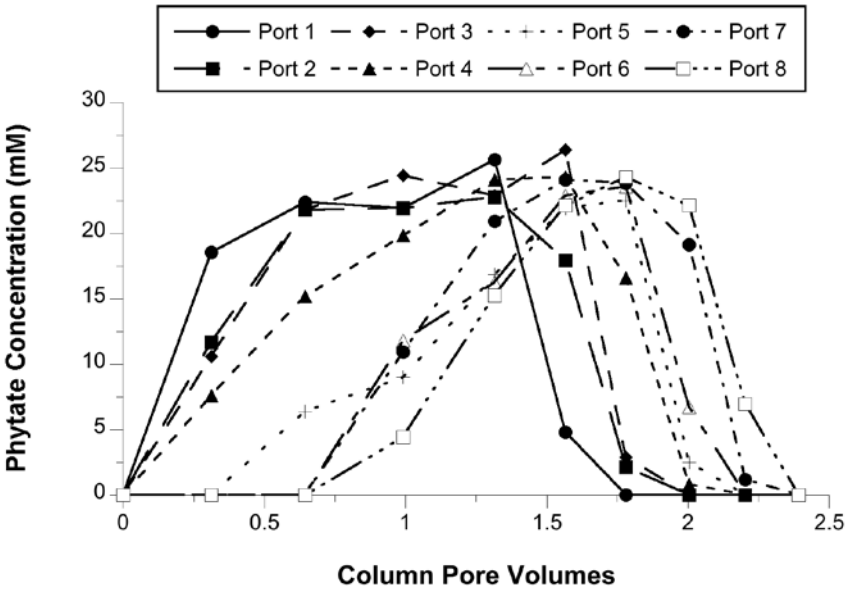


Figure 1-21. Concentration of phytate in each of eight ports compared to cumulative flow in a column of manganese-coated sand treated with 5% H_2O_2 stabilized by 25 mM phytate

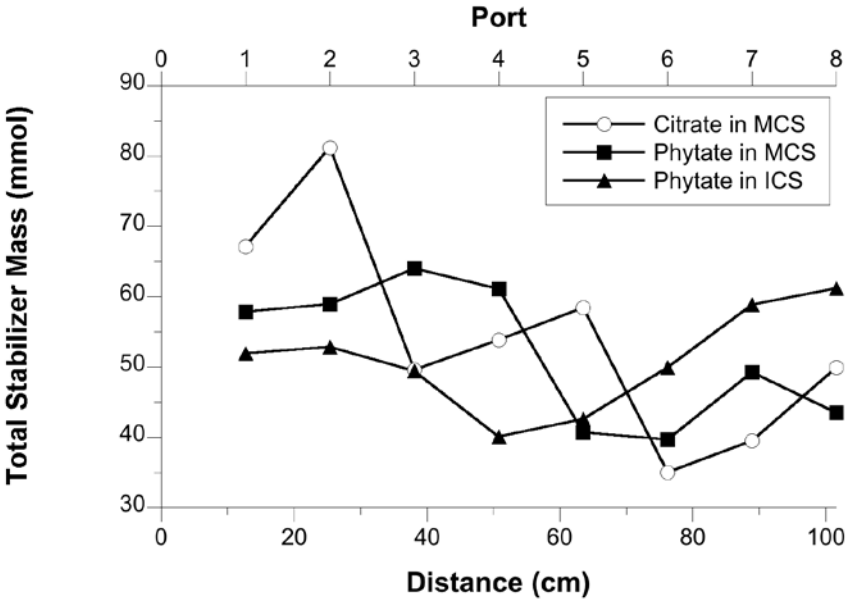


Figure 1-22. Total stabilizer mass measured at each of eight ports in columns containing iron-coated sand (ICS) and manganese-coated sand (MCS)

1.2.8 Flow Rates in Stabilized Hydrogen Peroxide Columns

The cumulative flow rates of the columns under the different experimental conditions are shown in Figure 1-23. Flow rates decreased over time in all of the columns; however, higher overall flow rates were maintained in both ICS and MCS columns containing stabilizers. The unstabilized ICS column had lower flow rate than the phytate stabilized column at all time points, while flow in the unstabilized MCS column decreased dramatically after 45 min. Plugging can be a significant problem in the application of CHP in the field, often through the gases and precipitation produced by CHP reactions. The higher flow rates in the stabilized columns are likely due to lower gas production and inhibition of precipitation through complexation of soluble iron and manganese in the systems. The results of this research demonstrate that stabilization of hydrogen peroxide using citrate and phytate not only lowers the rate of hydrogen peroxide decomposition in model subsurface systems, but may also minimize plugging of the subsurface.

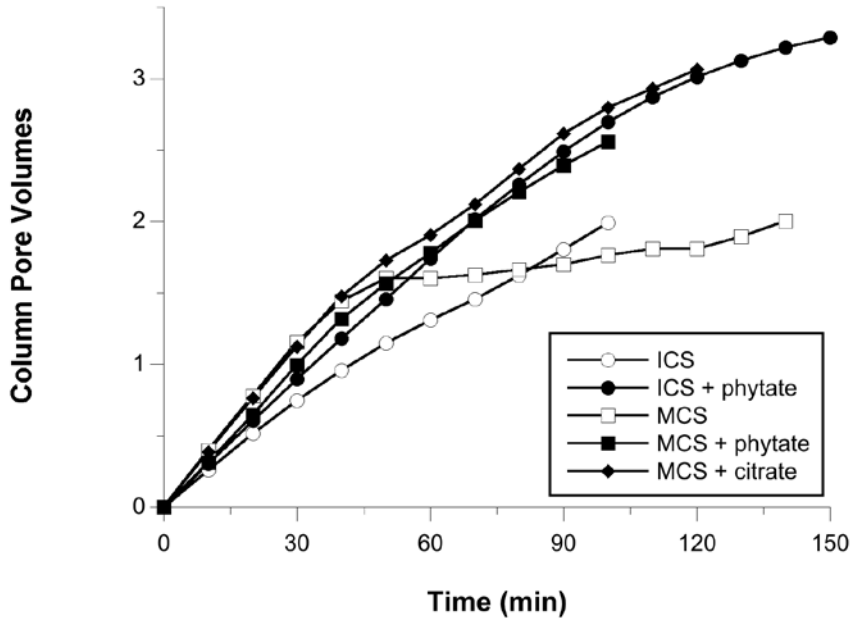


Figure 1-23. Flow rate with time in columns containing iron-coated sand (ICS) with and without phytate, and manganese-coated sand (MCS) with and without phytate or citrate

1.3 Conclusions on Hydrogen Peroxide Stabilization

The rapid rate of hydrogen peroxide decomposition in the subsurface represents the greatest limitation in the use of CHP for subsurface remediation. The stabilization of hydrogen peroxide using citrate, malonate, and phytate was studied in batch systems containing subsurface solids and one-dimensional columns containing iron oxide and manganese oxide coated sand. The results of this research demonstrate that hydrogen peroxide can be stabilized by up to 50 times using the stabilizers phytate, citrate, or malonate with minimal effect on the generation of reactive oxygen species. The most effective stabilizer for extending hydrogen peroxide half-life in most systems was phytate. However, citrate and malonate were as effective as phytate in promoting the CHP destruction of HCA, and more effective than phytate at promoting CHP destruction of hexanol. Another advantage of the use of stabilizers is the potential ease of delivery; under current practice, acid, soluble iron, or iron chelates are first injected into the subsurface followed by a second delivery of hydrogen peroxide. Use of the stabilizers may provide the potential for treatment using a single injection; hydrogen peroxide and the stabilizer could be mixed in a supply tank and injected into the subsurface together. Although 1 M or 10 mM concentrations of the stabilizer were used in this study, treatability studies should be conducted to determine the most effective stabilizer concentration for a specific contaminated site. Effective contaminant treatment and DNAPL destruction will likely be as effective in full-scale stabilized applications as in unstabilized applications, but with the benefit of better transport and contaminant contact with stabilized hydrogen peroxide.

Hydrogen peroxide was applied to the ICS and MCS columns at an initial concentration of 5% without stabilization and with stabilization by 25 mM citrate and 25 mM phytate at neutral

pH. Both citrate and phytate were effective stabilizers for manganese-coated sand, increasing hydrogen peroxide residuals by four-fold over unstabilized hydrogen peroxide. Although citrate was not an effective hydrogen peroxide stabilizer for iron-coated sand, phytate was extremely effective, increasing hydrogen peroxide residuals two orders of magnitude over unstabilized hydrogen peroxide. The concentrations and masses of the stabilizers did not change over time during column operation, which shows that the stabilizers will not lose their effectiveness after injection into the subsurface. Furthermore, flow rates in the columns with stabilizers were significantly higher than in the unstabilized systems, indicating that stabilizers may minimize plugging. Because of the increased lifetime of stabilized hydrogen peroxide, the treatment radius of influence in the subsurface during ISCO may increase significantly. These results provide promise for increased effectiveness and decreased cost in the application of CHP ISCO. Citrate and phytate stabilization appears to be mineral specific; therefore, a matrix of treatability studies using site-specific samples will need to be conducted for each site to determine the most effective stabilizer and its concentration.

2 Treatability Study Plan

2.1 Introduction

Treatability studies have been used extensively to design industrial waste treatment systems. For example, column studies are used in conjunction with bed depth service time (BDST) analysis to design full-scale activated carbon systems. Similar approaches are used for the design and scale-up of air strippers, ion exchange systems, precipitation reactors, and many other treatment processes. Such treatability studies provide definitive data on system dimensions and reagent dosages using linear or non-linear scale-up. Designing these processes without the data provided by treatability studies is impractical and not given consideration by process engineers. Treatability studies also benefit in designing in situ treatment processes such as In Situ Chemical Oxidation (ISCO).

Although treatability studies have undisputed benefits for the design of ex situ processes, the variability inherent in the subsurface makes it nearly impossible for completely mixed bench-scale systems to predict what will occur in the field during the implementation of CHP ISCO. However, ISCO treatability studies can provide information related to oxidant longevity and potential high rates of oxidant consumption, whether the contaminants of concern (CoCs) can be destroyed in the subsurface matrix, and the most effective stabilizer to apply in the field. Spacing of injection wells and the corresponding radius of influence (ROI) plays a significant role in the success of CHP ISCO deployment. Therefore, an additional goal of stabilized CHP treatability studies is to estimate the ROI for field application. In summary, the goal of ISCO treatability studies is to evaluate 1) hydrogen peroxide decomposition rate, 2) optimal stabilizer for hydrogen peroxide longevity, 3) contaminant destruction, 4) hydrogen peroxide and stabilizer

transport in the aquifer solids, 5) the effect of the optimal hydrogen peroxide formulation on permeability of the aquifer solids, and 6) estimation of the ROI for field application.

The desirable endpoint of the treatability study is to have enough oxidant in contact with the CoCs for a long enough period of time to promote its destruction. In other words, the goal of the treatability study is to determine the concentration of hydrogen peroxide and stabilizer that is best to achieve this goal.

2.2 Treatability Study Work Plan

2.2.1 General Approach

The treatability study is a comprehensive effort that will include a range of hydrogen peroxide concentrations and types and concentrations of stabilizers and activators. After the treatability study is completed, the dosage of hydrogen peroxide and stabilizer used in the field are available for field personnel. Specific performance objectives of a treatability study are listed in Table 2-1. A flowchart depicting the treatability study is shown in Figure 2-1.

2.2.2 Preliminary Evaluation of Sample Characteristics

A primary consideration of treatability studies is the number of samples on which the treatability study needs to be performed. Most sites for which ISCO is being proposed will have already been through a remedial investigation/feasibility study (RI/FS). Therefore, site maps with contaminant profiles and borehole loggings are assumed to be available. One core of subsurface solids should be collected from each region of areal heterogeneity to evaluate the effects of the solids on hydrogen peroxide decomposition rate and reactions. Subsurface solids are collected using standard procedures, such as Geoprobes. In general, sites with extremely homogeneous geochemistry require fewer samples, which can be composited. If the site exhibits

even a moderate degree of heterogeneity, individual lithologies will require separate treatability studies. Subsurface cores should be inspected visually for gross changes in organic matter and mineralogy, particularly iron oxides. Visual inspections can be used to help assess changes in lithology and associated changes in the reactivity of the oxidant between the lithologic units. Differences in subsurface solid reactivity with oxidants can also be determined by the visible decomposition of hydrogen peroxide, which provides visual indication of reactive mineralogy. Rapid hydrogen peroxide decomposition correlates primarily with the presence of manganese oxides and oxyhydroxides in the subsurface solids. Iron oxides and oxyhydroxides provide the next level of catalytic activity. If well cuttings are available, adding 5%–10% hydrogen peroxide to the well cuttings provides a valuable first-cut evaluation of the potential for CHP ISCO. If very little oxygen evolution and frothing occur (Figure 2-2a), hydrogen peroxide will be relatively stable when injected for CHP ISCO. However, if extensive oxygen evolution and frothing occur (Figure 2-2b), sufficient stabilization may not be possible for effective CHP injections. The metric for requiring subsamples between cores is a change of 25% in oxidant consumption rate between samples. If these visual inspections confirm site heterogeneity, batch and column treatability studies will be required for each of the different subsamples.

After the solids and groundwater are shipped to the treatability lab, a series of 30 g samples are weighed into 40 ml volatile organic analysis (VOA) vials. The water content of saturated solids is first determined. The volume of groundwater required to cover the 30 g of subsurface solids is determined by adding 0.5 ml increments of groundwater until the solids are covered. Oxidant consumption studies are then conducted using that volume of groundwater.

Table 2-1. Specific Performance Objectives of a Treatability Study and How These Performance Objectives Are Met

Performance Objective	Data Needs	Data Acquisition	Data Analysis
Limits of oxidant concentrations	Hydrogen peroxide concentration that provides temperature increase to no more than 40˚C. Persulfate concentration so that <50% is consumed in 7 days.	Default hydrogen peroxide concentration for plume samples is 5%. Default hydrogen peroxide concentration for source area is 11%. If temperature increase is greater than 40˚C for the default concentration in the presence of subsurface solids, lower hydrogen peroxide concentration until temperature increase in no more than 40˚C. Persulfate concentrations aree measured at 7 days.	Tabulate maximum temperature in reactors with default concentration or lower hydrogen peroxide concentrations as needed. Compare 7-day persulfate concentration to initial concentration.
Conditions for the treatment of dissolved vs. sorbed/DNAPL (source zones) compounds	Distribution of CoCs between aqueous and sorbed/NAPL phases	Plume samples are treated with dilute concentrations of oxidant (5%). Source areas would be treated with more concentrated oxidant solutions (11%).	Concentrations of CoCs in the dissolved and solid phases are tabulated.
Conditions that provide for effective (>99%) contaminant loss	Initial concentration of CoCs and concentration at the end of the reactions.	The initial concentration of CoCs in both groundwater and subsurface solids is assessed before the treatability study is begun. Groundwater and subsurface solids are be extracted with an organic solvent (e.g., hexane) and analyzed for the CoCs by gas chromatography/electron capture detection. Subsurface solids and groundwater are treated in VOA vials and vials are extracted and analyzed for contaminant loss.	CoC concentrations are compared to control systems. The metric for this performance objective is 99% CoC loss.

Table 2-1, Continued

Performance Objective	Data Needs	Data Acquisition	Data Analysis
Most effective stabilizer and its concentration for CHP treatment	Evaluate citrate, malonate, and phytate as stabilizers	A range of stabilizer concentrations are evaluated in batch studies for process conditions that result in > 99% CoC destruction. Hydrogen peroxide concentrations are quantified over at least three half-lives.	Hydrogen peroxide concentrations are plotted as a function of time and as semilog plots. The stabilizer concentration that provides the longest lifetime while promoting >99% CoC destruction is the metric for optimal process conditions.
Transport of stabilizer with hydrogen peroxide	Determine if stabilizer is in contact with hydrogen peroxide	Conduct column studies and measure hydrogen peroxide and stabilizer concentrations at sampling ports in 2m column.	Concentration data for stabilizer are plotted against concentration data for hydrogen peroxide. Best result: stabilizer concentration profiles coincide with hydrogen peroxide concentration profiles.
Effect on aquifer solids permeability	Determine if optimum hydrogen peroxide formulation will clog aquifer solids	Conduct column studies and measure seepage velocity and solids characteristics.	Seepage velocity in hydrogen peroxide systems is compared to control systems. Best result: no loss of seepage velocity with hydrogen peroxide treatment.
Radius of Influence	Hydrogen peroxide concentrations as a function of column depth	Conduct column studies and measure hydrogen peroxide concentration with column depth. Quantify solution residence time using bromide tracer.	Calculate first order hydrogen peroxide decomposition rate after peak concentration is achieved. Using rate constant, determine required hydraulic residence time. Multiply by pore water velocity to obtain ROI.

Figure 2-1. Flow chart of treatability experiments

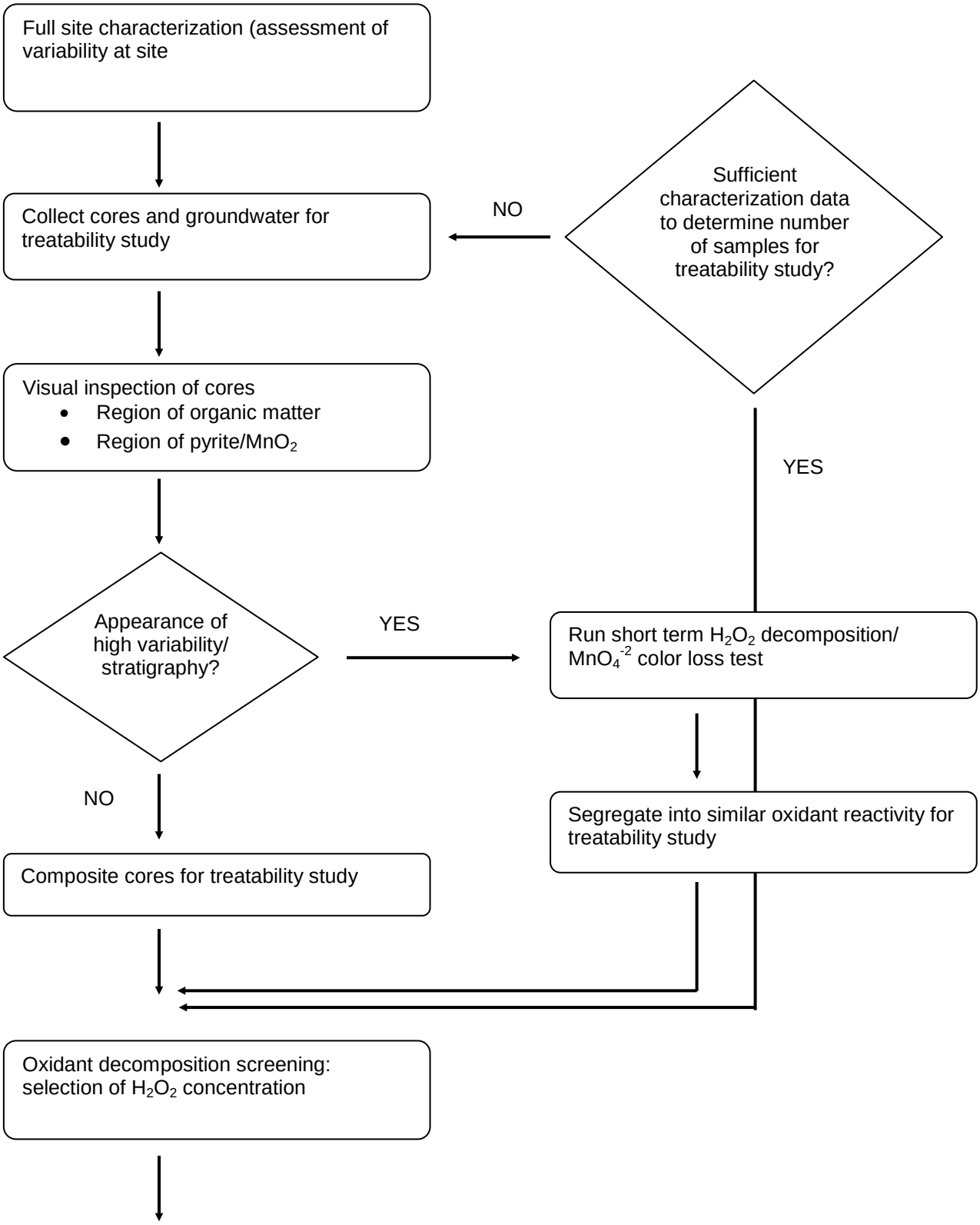


Figure 2-1, cont.

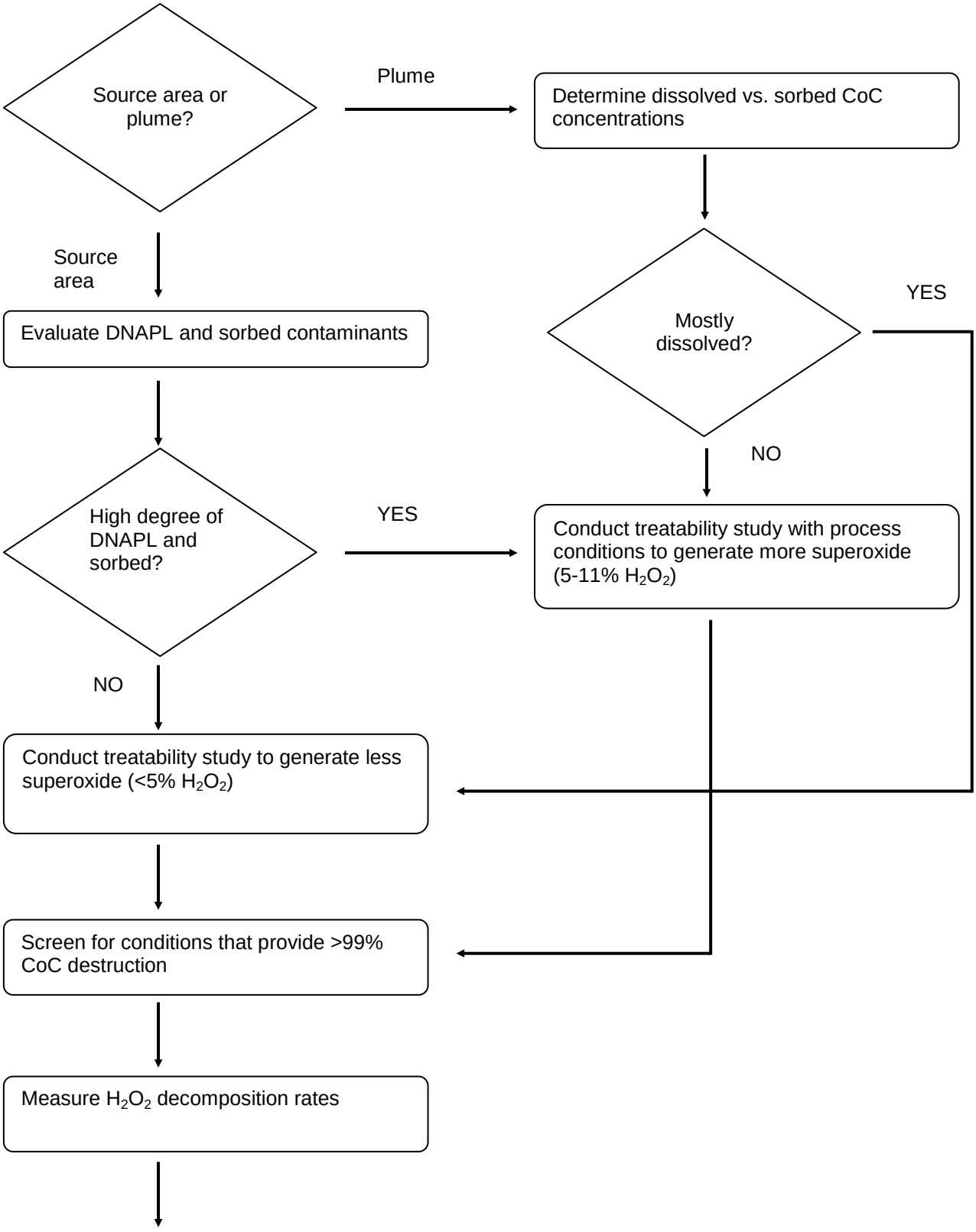
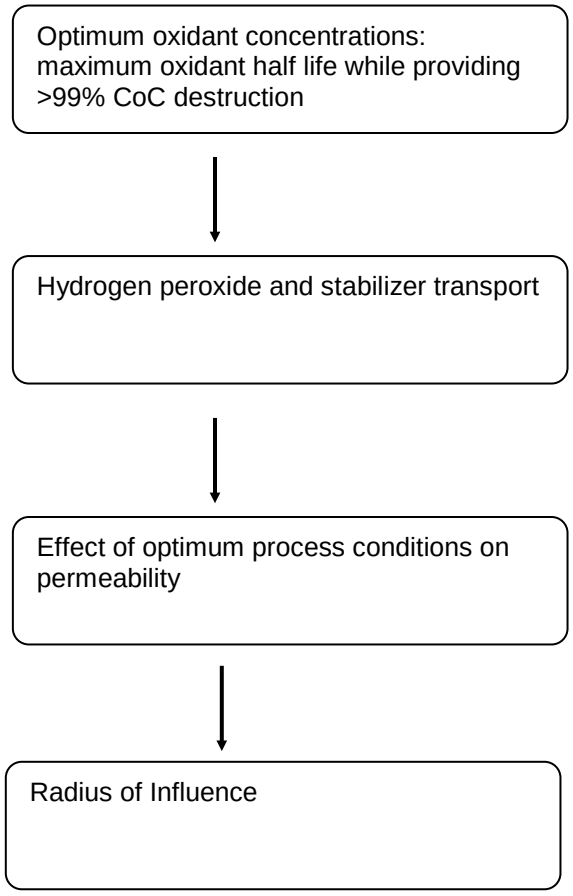


Figure 2-1, cont.



a

b

Figure 2-2. Visual inspection of subsurface solids-hydrogen peroxide slurries with a) slow hydrogen peroxide decomposition, and b) rapid hydrogen peroxide decomposition.

2.2.3 Stage 1: Initial Screening of Rate of Hydrogen Peroxide Consumption

Hydrogen peroxide has characteristics related to limitations on its concentrations. High concentrations of hydrogen peroxide in the presence of aquifer solids can result in extreme temperature increases to the point of boiling. When the temperature increases above 40˚C, hydrogen peroxide decomposition rates and temperature increases accelerate, and the hydrogen peroxide can decompose completely within minutes.

The initial screening of hydrogen peroxide is conducted in 40 mL VOA vials containing subsurface solids saturated with groundwater from the site. All vials containing the subsurface solids and groundwater are equilibrated in a water bath at 25˚C. The initial hydrogen peroxide concentration is 11% (the lower limit of adiabatic decomposition). CHP formulations are added to the systems, and residual hydrogen peroxide and temperature are monitored over 7 days. CHP formulations include mineral-catalyzed reactions stabilized by phytate, citrate, or malonate (10 mM) at neutral pH. For CHP reactions, if the maximum temperature attained in the reaction is > 40˚C, hydrogen peroxide concentrations are successively lowered by 1% until the maximum temperature in the system is ≤ 40˚C. After the maximum hydrogen peroxide concentration is obtained based on temperature increases, the residual hydrogen peroxide concentrations quantified over time are used to calculate half-lives under the various process conditions. The data from these screening studies are used to eliminate any process condition (i.e., hydrogen peroxide concentration with a specific stabilizer) from further consideration in which the hydrogen peroxide consumption is too great. Based on the experience of the project team, hydrogen peroxide decomposition rates that result in undetectable concentrations in < 24 hr are considered too high.

2.2.4 Stage 2: CoC Destruction Studies

CoCs are first quantified in the samples collected from the field. The CoCs are then tracked as the treatability study proceeds.

Source zone vs. plume treatment. Samples that have a higher proportion of CoCs in the sorbed and NAPL phases will require a higher flux of superoxide to desorb the sorbed material and to disrupt and destroy the NAPL globules and ganglia. Superoxide is generated through heterogeneous catalysis of hydrogen peroxide on the surfaces of most naturally occurring metal oxides in the subsurface. Therefore, the most effective pathway for the generation of a higher flux of superoxide is through the use of higher concentrations of hydrogen peroxide. Based on this conceptual framework, samples that have sorbed contaminants or NAPLs will require higher hydrogen peroxide concentrations. Hydrogen peroxide concentrations of $\leq$ 5% are effective in treating dissolved phase contaminants, while the treatment of sorbed contaminants and NAPLs requires hydrogen peroxide concentrations of 5-11% (Watts and Teel, 2005). In addition, treatability reactors need to be established with hydrogen peroxide concentrations representative of the concentrations that will be found downgradient as a result of decomposition (e.g., 0.1%, 0.2% hydrogen peroxide concentrations). CoC destruction promoted by such low hydrogen peroxide concentrations will provide a measure of effectiveness downgradient from the point of injection.

Treatability study reactions can be conducted in VOA vials with Teflon caps fitted with a port through which off gas escapes through an ORBO 32 gas adsorbent tube. Prior to starting the treatability reactions, vials containing the solids-groundwater samples are spiked with a concentration of the CoC equal to that of the measured concentration present in the site samples. The samples are extracted with an appropriate solvent (e.g., hexane for chloroaliphatics) and

recovery of the spiked contaminant are quantified to determine extraction efficiency. All reaction vials are established in duplicate to provide a measure of variance of data. Parallel are used to measure temperature and to monitor hydrogen peroxide concentration to determine when the reactions are complete. Control systems containing deionized water in place of the hydrogen peroxide solution are run in parallel to all treatment reactions.

CHP process conditions. A number of process conditions can be used to evaluate contaminant destruction in the subsurface solids-groundwater matrix. Three stabilizers may be employed in separate treatability tests. Catalysts are the naturally occurring minerals in the subsurface solids. Due to the high degree of site specificity in the stabilization of hydrogen peroxide, all three of the stabilizers (citrate, malonate, phytate) should be evaluated for contaminant destruction. Stabilizer concentrations will vary from 0.5 mM to 10 mM. With each stabilizer, a range of hydrogen peroxide concentrations should be used based on initial screening (Stage 1) and whether a source or a plume is being treated, providing a two dimensional factorial design.

Analysis. When the reactions are complete, separate vials are extracted with an appropriate solvent (e.g., hexane for chloroaliphatics); the extracts are then analyzed by gas chromatography (GC) or liquid chromatography (LC). CoCs may be analyzed using standard EPA methods (Table 2-2) or by in-house methods developed by the treatability study laboratory. Hydrogen peroxide residuals are evaluated using iodometric titrations as a function of time in parallel batch systems to estimate the potential lifetime of the hydrogen peroxide in the subsurface.

Table 2-2. Common SW-846 Methods for the Analysis of Contaminants of Concern (http://www.epa.gov/wastes/hazard/testmethods/sw846/online/index.htm)

Contaminants	SW-846 Method
Nonhalogenated organics	8015C
Aromatic and halogenated volatiles	8021B
Phenols	8041A
Phthalate esters	8061A
Nitrosamines	8070A
Organochlorine pesticides	8081B
Polychlorinated biphenyls	8082A
Explosives	8095
Polynuclear aromatic hydrocarbons	8100
Aniline and derivatives	8131
Organophosphorous compounds	8141B
Chlorinated herbicides	8151A

Confirmation of contaminant destruction. A comprehensive mass balance quantifying degradation products and elucidating degradation pathways is beyond the scope of treatability studies. However, some procedures are used to confirm contaminant destruction. First, ORBO tube analyses will provide a measurement of contaminant volatilization. Chloride can be measured for the more effective reaction conditions as a relatively straightforward procedure for quantifying destruction of chlorinated organics. Once the optimum treatment conditions are established, the reactions should be repeated. Split samples are collected and sent a separate laboratory for confirmation of the treatability study results.

2.2.5 Stage 3: Hydrogen Peroxide Longevity

The process condition that promotes > 99% destruction of chloroaliphatic CoC (the metric for treatment effectiveness) is then evaluated for hydrogen peroxide longevity. The reactions are established in the same manner as the Stage 2 procedure, and hydrogen peroxide is monitored over three half-lives. The metric for optimal process conditions is the stabilizer that provides the longest hydrogen peroxide half-life. The optimum process condition for each subsample is then used to evaluate transport of the hydrogen peroxide in concert with the stabilizer and changes in permeability through Stage 4 column studies.

2.2.6 Stage 4: Column Studies to Evaluate Hydrogen Peroxide Formulation Transport, the Effect of the Hydrogen Peroxide Formulations on Aquifer Permeability, and the Radius of Influence

As with other treatment processes that are mass transfer-limited, dynamic treatability studies are helpful in evaluating potential ISCO treatment effectiveness prior to field implementation. Column studies comprise the final segment of the treatability study. Column studies are performed using the optimal process condition for CHP and activated persulfate based on the metric of > 99% CoC destruction, maximum oxidant half-life, and the presence of only dissolved contaminants vs. contaminants with source zone characteristics (i.e., smear zones, sorbed contaminants). Column studies are also performed on each of the heterogeneity-based subsamples.

Teflon-lined columns (typically 10 cm diameter x 2 m high with sampling ports every 25 cm) are filled with subsurface solids from the field site. They are packed to provide the same groundwater flow velocity as the *in situ* solids by conducting tracer tests using bromide as a tracer to determine travel time through the column. If the column does not represent the same

groundwater flow velocity measured in the field, it should be repacked. The column treatability tests are run under saturated conditions to best represent existing field conditions. The columns are fed with groundwater collected from the site. The columns are prepared, the flow rate checked, and the columns fed with hydrogen peroxide the stabilizer. Samples are collected from each port over time as the study proceeds, and hydrogen peroxide concentration, stabilizer concentration, contaminant concentration, and pH are quantified. If some aspect of effective treatment is not met (e.g., hydrogen peroxide lifetime or contaminant destruction does not match what was predicted from batch studies), then batch study data and column design should be re-evaluated, and the column study repeated. When the flow through study is completed, aquifer solids should be collected from the sampling ports and analyzed for total contaminant residual, as well as for standard soil properties (e.g., particle size distribution, organic carbon content, cation exchange capacity, amorphous and crystalline iron and manganese oxides).

Changes in seepage velocity through the column will also be monitored and compared to control columns that received groundwater only instead of the hydrogen peroxide solution. If the seepage velocity decreases by more than 25%, rapid screening should be conducted in smaller columns (5 cm diameter x 0.5 m high) to isolate the parameter that is decreasing aquifer permeability (e.g., the hydrogen peroxide, stabilizer, etc.). Once the formulation component that is lowering the permeability is isolated, its concentration is varied in small column test to determine a concentration that does not affect permeability. The radius of influence (ROI) or field injections can also be estimated. The procedure for estimating the ROI, which is similar to the procedure developed by Gavaskar et al. (2000) for permeable reactive barrier column studies, is outlined in Table 2-3.

Table 2-3. Procedure for Determining the Radius of Influence of Injection

Step	Action	Calculation
1	Based on the bromide tracer study, determine the groundwater flow rate in the columns	
2	Using the H_2O_2 decomposition data, determine the time for H_2O_2 concentrations to decompose from the initial concentration to 0.3% (the minimum concentration at which both hydroxyl radical and superoxide are generated). This H_2O_2 lifetime can be determined graphically from sampling port data or by determining a first order rate constant and then solving for time using the first order rate expression:	$\ln C/C_0 = kt$ where $C = 0.3\%$ H_2O_2 C_0 = concentration of H_2O_2 injected k = first order rate constant for hydrogen peroxide decomposition ($day^{-}1$) t = lifetime of H_2O_2 (days)
3	Using the groundwater flow velocity, calculate the radius of influence:	$ROI = V_x \bullet t$ where V_x = pore water velocity (m/d) t = lifetime of H_2O_2 (days)

2.3 Endpoints of the Treatability Study

The optimum conditions from the column studies should be the starting point for conditions for treatment in the field. Within a treatability study report, the following endpoints should be used for the design of the pilot or full scale field study.

- The hydrogen peroxide concentration to be delivered to the subsurface
- The minimum hydrogen peroxide concentration at which contaminant degradation will proceed
- The most effective stabilizer and its concentration for CHP
- An estimate of the radius of influence (ROI)

3 Guidance for Field Application of CHP Stabilization

CHP is a broad-based oxidation system that is able to treat a wide range of organic contaminants including aromatics, polycyclic aromatic hydrocarbons (PAHs), and chlorinated and non-chlorinated alkenes and alkanes. CHP is based on the reactions of a variety of active oxygen species including the well-known hydroxyl radical (OH•), perhydroxyl radical (HO_2•), superoxide radical anion (O_2•$^-$), and hydroperoxide anion (HO_2^-). The utility of CHP is a function of the generation of a variety of active species beyond the well-known hydroxyl radical: hydroperoxide, the conjugate base of hydrogen peroxide, is a strong nucleophile; perhydroxyl radical is another oxidant; superoxide is a nucleophile and a reductant (Watts and Teel, 2005). The formation of and reactivity of these other active species is a function of the soil mineralogy, aqueous pH, dissolved anions and cations, and the hydrogen peroxide concentration and longevity.

3.1 The Need for Stabilizers

Despite its near-universal reactivity, CHP has had limited use for the remediation of soil and groundwater. This is due, to a great extent, to the perceived lack of stability of hydrogen peroxide in many soils limiting both transport and reactivity. The perceived instability of hydrogen peroxide has led to increasing use of sodium persulfate ($Na_2S_2O_8$) instead of hydrogen peroxide due to its greater stability. Sodium persulfate is another peroxygen compound with a typical half-life of 10 to 20 days versus a typical half-life for hydrogen peroxide of 1 to 2 days.

The application of CHP for remediation requires consideration of its rate of decomposition; hydrogen peroxide can decompose to oxygen and water and generate significant

heat. The heat of decomposition of hydrogen peroxide is approximately 23,000 cal/mol H_2O_2.

$$2H_2O_2 \rightarrow O_2 + 2H_2O + \Delta \quad (3\text{-}1)$$

The heat that is generated can accelerate the rate of hydrogen peroxide decomposition. At a concentration of about 11%, the abiotic decomposition of hydrogen peroxide can generate enough heat to reach the boiling point of water. Under some conditions, due to decomposition, hydrogen peroxide may have a half-life of a few minutes. This limits the transportability of hydrogen peroxide. The shorter the half-life of peroxide, the shorter is the radius of injection.

Hydrogen peroxide decomposition is caused by several factors that are often considered during treatability studies. The primary factor driving hydrogen peroxide decomposition is the presence of catalytic minerals, particularly manganese oxides, which are present in the matrix as soil minerals and/or surface coatings. The second factor is the form of the metal oxide – amorphous or crystalline. Amorphous metal oxides tend to be more active decomposition catalysts. The third factor is the surface area of the soil matrix. Generally, the greater the surface area of iron or manganese enriched soils, the greater the rate of decomposition.

As discussed in the previous sections and above, the focus of this document is on the use of stabilizers to increase the half-life of hydrogen peroxide. By increasing the half-life, stabilized CHP increases the persistence and transportability of hydrogen peroxide to provide increased treatment time and distance in the subsurface. Modern hydrogen peroxide stabilization was developed by Watts et al. (2007), who screened 11 organic compounds. Of these, three were found to increase the stability of hydrogen peroxide: citrate, malonate and phytate. (see Figure 1-1). The results of the study of the three stabilizers are summarized in Table 3-1:

Table 3-1. Summary of Stabilizer Test Results

Soil	Best Stabilizer	Concentration	Unstabilized H_2O_2 $T_{1/2}$, Hours	Stabilized H_2O_2 $T_{1/2}$, Hours
Georgia	Phytate	250 mMol	4	15
Maine	Phytate	250 mMol	1.5	32
California	Phytate	250 mMol	0.5	26
Washington	Citrate, Malonate, Phytate	250 mMol	4	22

In the study of peroxide stabilization four soils were studied. Phytate was shown to provide the best stabilization in three out of the four soils.

The unstabilized half-lives listed in Table 3-1 (column 4) show why the use of unstabilized hydrogen peroxide often results in a loss of effectiveness for the use of CHP. Half-lives of 0.5 to 1.5 hours, without stabilization, would generally make the application of CHP impracticable. Even a 4-hour half-life would be marginal for effective treatment. At short half-lives the hydrogen peroxide would not last long enough to have effective distribution or to react effectively with sorbed or nonaqueous phase liquid (NAPL) contaminants. By comparison, half-lives of 20 to 30 hours, resulting from effective stabilization, make the successful application of CHP highly feasible. Stabilization can increase the persistence of peroxide by 20 to 50 fold, which would increase the radius of injection and the ability to treat sorbed or NAPL contaminants.

3.2 Factors Affecting Successful Application of CHP

Successful application of CHP is defined as having enough hydrogen peroxide (active oxygen species) in contact with the contaminant for a long enough period of time for CHP to react effectively with the contaminants, achieving the desired endpoint of contaminant destruction. This definition is depicted in Figure 3-1. Effective delivery of the active oxygen species is central to the successful application of CHP and persistence is a key to effective delivery. Persistence affects the radius of injection: the greater the persistence, the greater the potential spacing between injection points. CHP persistence also affects the reactant dosing; i.e., the mass and concentration of hydrogen peroxide to be applied within a target treatment volume.

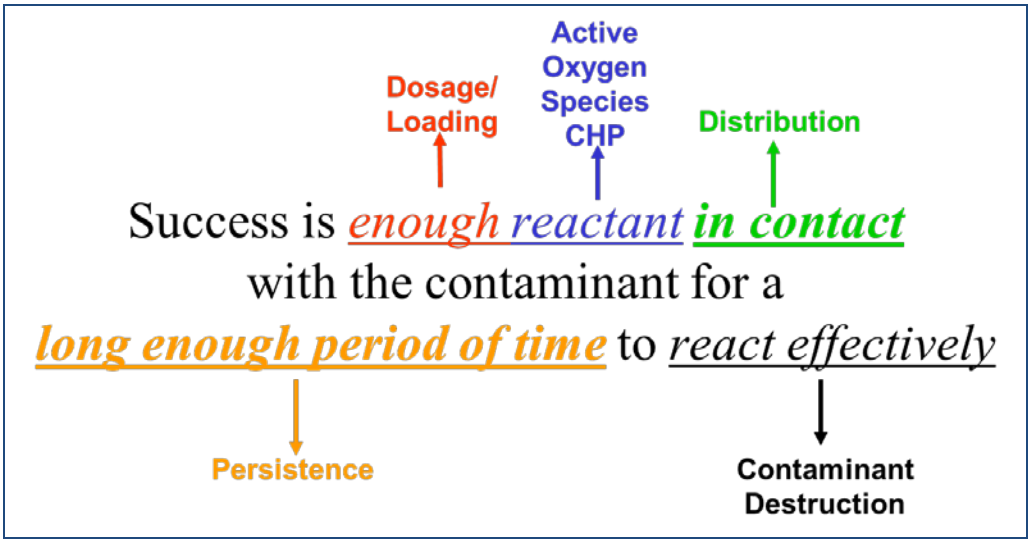


Figure 3-1. Factors affecting the successful application of CHP

3.2.1 Dosing

Dosing has a number considerations including:

- ***Stoichiometric demand.*** Stoichiometric demand is the mass of reactant needed to destroy the anticipated mass of contaminants calculated based on the equivalent weights of the

oxidant and of the contaminants in the treatment volume. The equivalent weight is the molecular weight divided by number of electrons transferred.

Calculating stoichiometric demand is illustrated by the reaction of hydroxyl radical with trichloroethylene (TCE):

$$H^+ + OH\bullet + e^- \rightarrow H_2O \quad (3\text{-}2)$$

$$Cl_2C{=}CHCl + 4H_2O \rightarrow 2CO_2 + 3HCl + 6H^+ + 6e^- \quad (3\text{-}3)$$

The equivalent weight of hydroxyl radical is 17 g/eq. The equivalent weight of TCE is 21.67 g/eq (130 g/mol ÷ 6e). Assuming (1) a TCE concentration of 100 µg/L and (2) a porosity of 25%, it would take 19.6 g of hydroxyl radical to treat 1 m^3 of aquifer. Given that one hydrogen peroxide molecule produces one hydroxyl radical, it would take 39.2 g of hydrogen peroxide per m^3 of aquifer to treat the TCE.

- ***Soil oxidant demand (SOD).*** Oxidants react with other reduced species present such as metal sulfides or soil organics, which is illustrated for pyrite (FeS_2):

$$2FeS_2 + 15H_2O_2 \rightarrow 2Fe(OH)_3 + 4H_2SO_4 + 8H_2O \quad (3\text{-}4)$$

Assuming a pyrite content of 100 mg/kg in the soil, the SOD could be as high as 300 g of added hydrogen peroxide to the peroxide demand for the treatment of TCE. Therefore, the soil oxidant demand can be several orders of magnitude higher than the stoichiometric demand.

- ***Decomposition.*** As illustrated in Equation (1), hydrogen peroxide decomposes to oxygen and water, which lowers the mass of hydrogen peroxide that is available to react with the contaminant. The rate of hydrogen peroxide decomposition is site specific and needs to

be measured during treatability testing. The impact of hydrogen peroxide decomposition on the effective utilization of hydrogen peroxide increases with distance from the injection point. Assuming a hydrogen peroxide half-life of 4 hours, an injection well spacing of 3 m, a radius of injection of 1 m, an injection concentration of 10%, and a groundwater velocity of 1 m/day, the loss due to decomposition of unstabilized hydrogen peroxide could be >75% per day.

The dosing is, therefore, strongly tied to the persistence of the hydrogen peroxide. Increasing the persistence of hydrogen peroxide in the application of CHP is predominantly a function of the choice and application of a stabilizer.

3.2.2 Delivery

The method of delivery is also a function of the persistence of the hydrogen peroxide. As discussed above, the half-life of peroxide for a given site will affect the design spacing of injection wells, the volume of hydrogen peroxide to be applied at each injection well, the concentration of peroxide used, and the rate of injection. There are two basic approaches to injection: emplacement and circulation. Emplacement is the rapid application of a hydrogen peroxide solution over the entire area to be treated. This usually involves pressurized injection, multiple injection wells, and injection intervals to directly emplace the solution in target locations. Emplacement involves discrete injection events, is independent of groundwater flow, and may be designed based upon site conditions and the spatial distribution of contaminant mass. In contrast, circulation is the longer duration application of hydrogen peroxide using injection (and pumping) and groundwater flow to convey and control the distribution within the area to be treated. Circulation distribution relies on ambient groundwater flow to convey solution and may be a continuous or batch process. If coupled with pumped recovery and recirculation by

injection, the rate of circulation within the target volume can be increased. Sites that promote rapid hydrogen peroxide decomposition typically use direct emplacement and shorter injection spacing, whereas sites with longer hydrogen peroxide half-lives (> 20 hours) can use circulation injection systems. Circulation systems are generally lower cost due to the decreased infrastructure required.

3.3 Health and Safety Considerations

The decomposition of hydrogen peroxide may present some health and safety concerns. As seen in Equation (3-1), the decomposition of hydrogen peroxide produces heat and oxygen. As the concentration of hydrogen peroxide increases, the temperature and gas volumes produced by the decomposition of hydrogen peroxide also increase. At 11% hydrogen peroxide, enough heat is released to boil water, and significant volumes of gas (O_2 and $H_2O_{(g)}$) are produced. At a 10% concentration of hydrogen peroxide, decomposition produces 45 L of gas per L of hydrogen peroxide, and at 20% hydrogen peroxide the gas volume produced is 300 L gas per L of hydrogen peroxide. The heat and gas volumes produced can cause rapid pressure release and mobilization of VOCs. “Geysers” of contaminated groundwater and mud have been observed at sites where 15 to 20% hydrogen peroxide was injected. Figure 3-2 shows rupture of asphalt due to pressure build-up during the injection of 25% hydrogen peroxide. Based on the danger of pressure ruptures there are several recommended guidelines:

1. All containers, tanks, and bottles with greater than 3% H_2O_2 should be vented.
2. All tubing, piping, valves, and pumps should be drained and flushed with water within one hour of pumping solutions greater than 3% H_2O_2.
3. The maximum injection concentration should be < 12% H_2O_2.

4. Hydrogen peroxide should be stored only in clean virgin containers until use; it should also be transferred by dedicated equipment and remain in vented chemically compatible containers (pre-passivated if necessary). Hydrogen peroxide solutions must be covered and kept clean of particulates (dust, leaves, etc.), which can create a catalytic reaction resulting in extreme rates of decomposition.
5. Hydrogen peroxide solutions must be stored in vented containers and piping at all times. Hydrogen peroxide solutions should never be trapped between values without the provision of vents.
6. Any spills of hydrogen peroxide should be immediately diluted to < 3% with clean water. Dilute solutions may be allowed to infiltrate into the soil without harm.

Figure 3-2. Rupture of asphalt due to rapid pressure release during injection of 25% H_2O_2

3.4 Guidance for the Field Application of Stabilization

This section presents an overview of the steps that need to be completed to evaluate and apply stabilized CHP processes during a remediation project. This section is not intended to be a

manual for the design and application of an ISCO/CHP project; references providing guidance for ISCO project planning and execution are available in other publications (ITRC 2001, 2005). Other ESTCP documents are available to assist in ISCO design and deployment including Development of a Design Tool for Planning Aqueous Amendment Injection System Soluble Substrate Design Tool (ER-200626) (http://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/ER-200626/ER-200626) and In Situ Chemical Oxidation for Groundwater Remediation—Technical Practices Manual (ER-200623) (http://www.serpd-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/ER-200623/ER-200623). The following discussion will assume that the decision to use CHP has been made. The relevant questions that remain include:

- Whether stabilization would be beneficial and, if so,
- What stabilizer, at what concentration, would be optimal.

It should be noted that there are several site specific conditions negating the use of CHP for contaminant treatment, even with the use of stabilization. These include the following:

- Contaminants that are not accessible to aqueous treatment agents because the contaminants are:
    - Distributed in low permeability strata of > 0.25 M in thickness such as clay or silty-clay.
    - Diffused into competent low permeability bedrock.
    - Randomly distributed in non-contiguous, interbedded silts, sands and clays.

- Contaminants that are not adequately delineated in soil, groundwater and vapor state to be able to design an effective treatment system.

- Contaminants that are distributed in a mineral-rich lithology with total iron and manganese > 5% by weight.

- Contaminants that have low reactivity to CHP.

- Contamination with limited accessibility due to shallow utilities or location under buildings.

Shear thinning fluids have recently been proposed to enhance the delivery of reagents into low permeability strata. If the site to be treated is characterized by low permeability strata, treatability studies could be conducted with the addition of biopolymer xanthan gum (Kelco Oil Field Group, 3300 Bingle Road, Houston, TX 77055, (713) 985-7575, Kofg.com). After the optimum stabilizer and stabilizer concentration is determined, column studies (Section 2.2.6) are repeated with biopolymer xanthan gum ranging from 200 mg/L to 1000 mg/L (Zhong et al., 2001). Both hydrogen peroxide concentrations and CoC concentrations would be tracked during the column tests.

3.4.1 Screening a Site for the Applicability of Stabilization

Assuming that the site is amenable to CHP, that the contamination is accessible, and that the contaminants can be degraded by CHP, the question is whether stabilization of the peroxide should be evaluated and/or applied. The detailed protocol for evaluating and designing a stabilization approach is discussed in Chapter 2, “Treatability Study Guidance.” The question is

whether there are methods to screen a site to know (1) that the treatability study is needed and (2) that stabilization will be beneficial.

Even stabilization of the hydrogen peroxide may not be beneficial if the decomposition is essentially instantaneous. Under such conditions, the hydrogen peroxide produces “vapor” or “froth” when added to the soil, precluding effective or safe injection with liquid-based pumping equipment. Under these conditions, the hydrogen peroxide may impart significant backpressure from the formation creating a subsurface gas-lock and hazardous conditions during the pumping application. The following guidance factors can be used for screening the potential need for and/or benefit of stabilization treatability testing.

- ***Site mineralogy.*** If a description or characterization of the site mineralogy indicates high iron and/or manganese oxide content, a treatability test could be beneficial.

- ***Soil color.*** If the soil is red, brown, or red with black lenses, a treatability test will be beneficial. The coloration indicates moderate to high levels of iron and manganese oxides under oxidizing conditions.

- ***Gas generation.*** A more accurate means of screening site soils for the potential benefit of stabilization is to measure the volume of gas generated over time after hydrogen peroxide is added to site soil. Figure 3-3 pictures the apparatus needed.

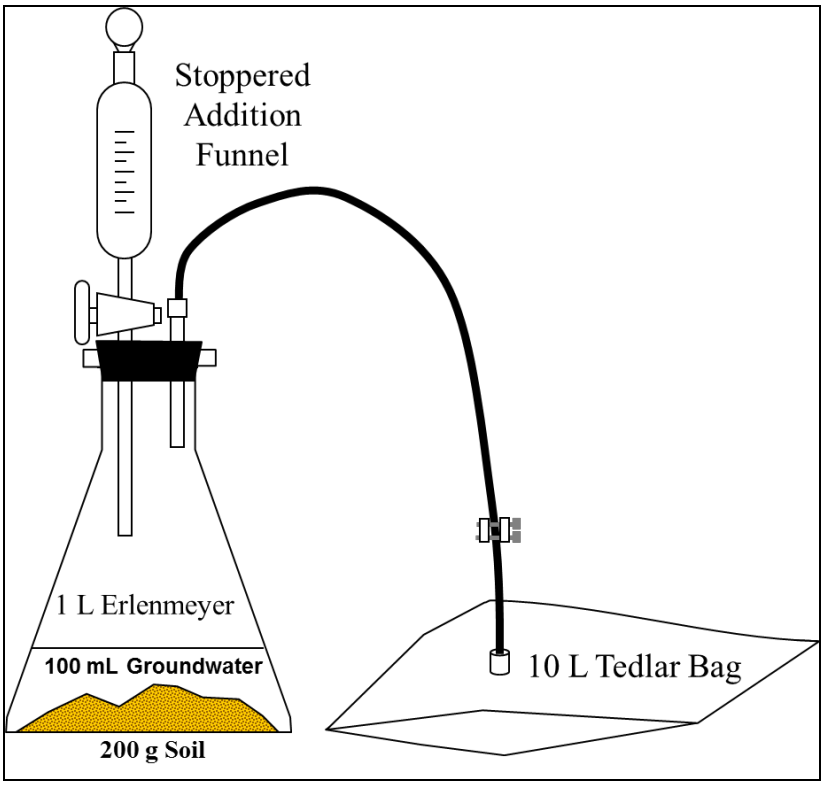


Figure 3-3. Apparatus for measuring gas generation

The Erlenmeyer flask is charged with 100 ml of site groundwater and a minimum of 200 g of site soil from the strata where hydrogen peroxide is injected. The soil and groundwater are allowed to equilibrate for an hour. A 100 ml volume of 10% hydrogen peroxide is added to the flask using a stoppered glass addition funnel. The peroxide is added over 15 minutes and the Erlenmeyer flask is periodically swirled. After the peroxide is added the gas volume in the Tedlar bag is measured at 1, 2, 4, 12, 24, and 48 hours or until no more gas is generated.. The theoretical gas volume for 100% decomposition is 4.5 L. If no gas is generated in 12 to 24 hours, the peroxide is stable and there is no need to further evaluate the use of stabilization.

The gas generation test can be repeated with the addition of 0.4 g of sodium phytate (5 mmol) to screen the effect of stabilization on the peroxide decomposition. If the addition of phytate (or other stabilizer) has no beneficial effect on peroxide decomposition it may indicate that stabilization is not feasible.

3.4.2 Stabilization Treatability Study

Chapter 2 of this document provides guidance for conducting robust treatability studies to evaluate stabilization. The goals of the treatability study are to determine:

- The hydrogen peroxide concentration to be delivered to the subsurface
- The minimum hydrogen peroxide concentration at which contaminant degradation will proceed
- The most effective stabilizer and its concentration for CHP
- Estimation of radius of influence

There are four stages recommended for the treatability study:

Stage 1: Initial screening of rate of hydrogen peroxide consumption

Stage 2: Contaminant destruction studies

Stage 3: Study of how to increase hydrogen peroxide longevity

Stage 4: Column studies to evaluate hydrogen peroxide transport, the effect of the hydrogen peroxide formulations on aquifer permeability, and the radius of influence of CHP (See Table 2-3)

Details of these stages are provided in Chapter 2.

3.4.3 Integration of Stabilization Test Results with CHP Design

The treatability testing for stabilization should ideally be conducted before the CHP design is completed. Stabilization will affect the design. Greater longevity for the peroxide can affect both the number and spacing of injection wells and the concentration and volume of hydrogen peroxide to be injected. Well spacing is directly related to the ROI. There should be a sufficient overlap of reagents; therefore, the spacing of injection wells should be < 2•ROI. The spacing of injection wells is open ended and subject to professional judgment, but should generally be no greater than 0.75•2•ROI. For example, consider an injection site of 100 m^2. If the radius of injection is 1.5 m, based on the unstabilized peroxide longevity, 14 injection wells would be needed to treat the area, If the longevity of the peroxide due to stabilization increases such that the radius of injection increases to 2.5 m, only 5 injection wells would be needed, resulting in a significant savings. Thus, the stabilization results would positively affect the design.

A number of parameters determined during the treatability testing will have a direct impact on the CHP design. These are listed in Table 3-2.

Table 3-2. Impact of treatability results on final design

Parameter Determined in Treatability Test	Impact on Design

H_2O_2 longevity (half-life)	• Radius of injection
	  ○ Injection well spacing
	  ○ Number of injection wells
	  ○ Number of applications of H_2O_2

Optimal H_2O_2 concentration for CoC destruction	• H_2O_2 dosing
	  ○ Concentration
	  ○ Volume
	  ○ Pore volume injected

CoC destruction efficiency	• Number of applications of H_2O_2
ROI	• Well spacing and number of injection sites

3.4.4 Performance Monitoring

Performance monitoring at field sites involves the measurement of stabilizer and oxidant concentrations over time to evaluate the persistence and reactivity of CHP. There are a number of factors that need to be monitored to evaluate and maintain performance. These include:

- Hydrogen peroxide decomposition rates: hydrogen peroxide concentration measured over time and distance
- Changes in geochemistry over time: dissolved metals, anions, pH, ORP
- Longevity and persistence of stabilizer over time and distance
- Contaminant destruction: a robust sampling program to measure contaminants over time and space
- Longevity of hydrogen peroxide over time and distance

- Permeability changes evidenced by injection rates, backpressure, and water table elevation

3.5 Field Pilot Test of Stabilization – Push-Pull Test

With complex sites there may be a benefit to running a field pilot test to verify the conclusions of the stabilization treatability testing. A test methodology that is easy to apply is a push-pull test. The steps in a push-pull test include:

1. 1000 L of groundwater are pumped at 10 L/min from an existing or newly installed monitoring well into a clean 2000 L tank. (Ideally soil from the newly installed well was used for the treatability testing.)
    a. Groundwater sample is collected every 250 L and analyzed for pH, temperature, TOC, and CoCs
2. The groundwater is amended with 30% hydrogen peroxide to a final concentration of 5%. After one hour, a water sample is collected and analyzed for pH, temperature, hydrogen peroxide, TOC, and CoCs.
3. The amended groundwater is pumped back into the well at 10 L/min.
4. Two hours after the amended groundwater is completely injected, the well is pumped at 10 L/min until 4000 L are removed.
    a. Groundwater sample is collected every 500 L and analyzed for pH, temperature, hydrogen peroxide, TOC, and CoCs.
5. The well is not operated for one week.
6. The test is repeated with 5 mM of a stabilizer (e.g., phytate) added with the peroxide (step 2).

a. The stabilizer and solution chemistry are based on the treatability testing.

The results of the tests are compared to determine the effect of stabilization on peroxide longevity and reactivity.

3.6 Summary

CHP has the potential to once more be a widely used effective remediation method for destruction of a wide range of organic contaminants. This will entail more routine treatability testing of peroxide stabilization in evaluating the use of CHP. This should be done as part of the overall design process.

The treatability testing described in this document is quite rigorous. It can, however be modified to meet site needs. Minimally the testing should determine/document the best stabilizer system and the optimal reaction conditions.

4 Case Histories

Several treatability studies have been conducted using stabilizers at the WSU Chemical Oxidations Laboratory. Two typical, but different, studies included a chemical manufacturing site in Michigan and a petroleum spill in Colorado.

4.1 Michigan Phytate-Stabilized Hydrogen Peroxide Treatability Study

4.1.1 Introduction

The industrial site in Michigan is contaminated with TCE, styrene, ethylbenzene, and toluene. The original focus of the treatability study was the use of hydrogen peroxide-activated persulfate. However, methodical evaluation of the effectiveness of persulfate vs. hydrogen peroxide and use of phytate as a stabilizer provided a different and more effective process design for treatment of the site.

4.1.2 Results

First set of persulfate/peroxide reactions. Two soils were treated in the study: Soil 1 was treated first, followed by Soil 2. The first phase treatment process conditions using Soil 1 are listed in Table 4-1, and the results of the first phase of treatment are listed in Table 4-2. Loss of all four contaminants in control systems was negligible. Hydrogen peroxide activation of persulfate (Treatment 1) was moderately effective in treating all four contaminants, with 23%–39% of the contaminants remaining. Treatment 2 conditions (hydrogen peroxide + persulfate + ferrous sulfate) were slightly less effective than Treatment 1. However, hydrogen peroxide + persulfate + phytate (Treatment 3) was highly effective, with only 9%–12% of the contaminants remaining. Base-activated persulfate (Treatments 4 and 5) was only moderately effective.

Table 4-1. Process Conditions for First Phase Treatments

Treatment 1	Treatment 2	Treatment 3	Treatment 4	Treatment 5
H_2O_2: Persulfate (10:1 molar ratio) 1.5% Sodium Persulfate	H_2O_2 : Persulfate (10:1 molar ratio) 1.5% Sodium Persulfate 200 mg/L Ferrous Sulfate	H_2O_2 : Persulfate (10:1 molar ratio) 1.5% Sodium Persulfate 5mM phytate	NaOH:Persulfate (2:1 molar ratio) 1.5% Sodium Persulfate	NaOH:Persulfate (6:1 molar ratio) 1.5% Sodium Persulfate

Table 4-2. Residual Contaminants During the First Phase Treatments for Soil 1

	Contaminant Residual (µg/L)				% Contaminant Remaining			
	TCE	Styrene	Ethyl-benzene	Toluene	TCE	Styrene	Ethyl-benzene	Toluene
Initial	380700	415500	6710	1180	100	100	100	100
Day 3								
Control	346500	423800	6580	1240	91	102	98	105
Treatment 1	202300	157900	2600	340	53	38	38	28
Treatment 2	267700	147000	3000	550	70	35	44	46
Treatment 3	107300	122200	2700	260	28	29	39	22
Treatment 4	278800	85700	4900	920	73	21	72	78
Treatment 5	268100	39800	4600	810	70	10	68	68
Day 6								
Control	331200	415500	6710	1210	87	100	100	102
Treatment 1	89600	143500	2700	270	24	35	39	23
Treatment 2	113000	149500	2800	360	30	36	41	30
Treatment 3	44500	39500	1000	120	12	9	14	10
Treatment 4	236300	55600	4800	960	62	13	71	81
Treatment 5	201800	16800	4300	780	53	4	64	65

Note: The contaminant concentrations are volumetric based. The reactors contained 20 g of soil + 6 mL of added groundwater. The total volume of the slurries was 20 mL.

Peroxygen residuals during treatment of Soil 1 are listed in Table 4-3. As expected, phytate-stabilized systems provided the highest peroxygen residuals at Day 3, and only base-activated persulfate systems provided detectable persulfate concentrations.

Table 4-3. Peroxygen Residuals in Soil 1 During the First Phase Treatments

Treatment	Hydrogen Peroxide (%)	Persulfate (%)
Day 3		
Treatment 1	0.4	0.4
Treatment 2	0.2	0.1
Treatment 3	0.9	1.8
Treatment 4	N/A	1.3
Treatment 5	N/A	0.7
Day 6		
Treatment 1	Nondetectable	Nondetectable
Treatment 2	Nondetectable	Nondetectable
Treatment 3	Nondetectable	Nondetectable
Treatment 4	N/A	1.1
Treatment 5	N/A	0.3

Second set of persulfate/peroxide reactions. After evaluation of the results of the first set of reactions, the treatability study team and project manager and his team proposed a second set of conditions in a conference call. The process conditions for treatments conducted under the second phase of the treatability study are listed in Table 4-4. The goal of the second set of treatments was to evaluate a more aggressive activation of persulfate by hydrogen peroxide and to compare hydrogen peroxide + persulfate to hydrogen peroxide without persulfate. Residual contaminants in Soil 1 after the second phase treatments are listed in Table 4-5. Loss of the contaminants in the control systems was negligible, with 88%–92% of the contaminants remaining after six days. Contaminant volatilization through capture in ORBO tubes was also negligible in these systems. Contaminant destruction was only minimally successful using

Treatment 1 (CHP–Persulfate + 1,000 mg/L ferrous sulfate) and Treatment 2 (CHP+ 1,000 mg/L ferrous sulfate), with 31%–63% of the contaminants remaining after six days. The ferrous sulfate likely decomposed hydrogen peroxide rapidly, resulting in less effective treatment. However, temperature increases were minimal, which is unexpected compared to the behavior of hydrogen peroxide in other soils. More effective contaminant destruction was observed with phytate addition (Treatments 3 and 4); the lower contaminant residuals (20%–36%) were likely due to a more sustained and therefore more effective reaction.

Similar trends are evident in the treatment of Soil 2 (Table 4-6). Treatments containing ferrous sulfate (Treatments 1 and 2) were less effective in contaminant destruction, with 7%–44% of the contaminants remaining, while treatments containing the stabilizer phytate (Treatments 3 and 4) resulted in contaminant residuals of 2%–25%. As with the results for Soil 1 (Table 4-5), a controlled and sustained CHP reaction with or without persulfate provided the most effective contaminant destruction.

Table 4-4. Process Conditions for Second Phase Treatments

Treatment 1	Treatment 2	Treatment 3	Treatment 4
10% Hydrogen Peroxide 1,000 mg/L Ferrous Sulfate 1.5% Sodium Persulfate	10% Hydrogen Peroxide 1,000 mg/L Ferrous Sulfate	10% Hydrogen Peroxide 5 mM Sodium Phytate 1.5% Sodium Persulfate	10% Hydrogen Peroxide 5 mM Sodium Phytate

Table 4-5. Residual Contaminants in Soil 1 After Second Phase Treatments

	Contaminant Residual (µg/L)			% Contaminant Remaining		
	TCE	Styrene	Ethylbenzene	TCE	Styrene	Ethylbenzene
Initial Conc.	170800	468900	8800	100	100	100
Day 3						
Control	155500	445500	8500	91	95	96
Treatment 1	90600	201700	4670	53	43	53
Treatment 2	112800	234500	4580	66	50	52
Treatment 3	51300	98500	3350	30	21	38
Treatment 4	56400	140700	3000	33	30	34
Day 6						
Control	150300	431400	7920	88	92	90
Treatment 1	87200	145400	3610	51	31	41
Treatment 2	107700	234500	4490	63	50	51
Treatment 3	53000	93800	3000	31	20	34
Treatment 4	61500	112600	2910	36	24	33

Table 4-6. Residual Contaminants in Soil 2 After Second Phase Treatments

	Contaminant Residual (µg/L)			% Contaminant Remaining		
	TCE	Styrene	Ethylbenzene	TCE	Styrene	Ethylbenzene
Initial Conc.	650	110600	45500	100	100	100
Day 3						
Control	610	111700	43700	93	101	96
Treatment 1	90	33200	10100	13	30	22
Treatment 2	90	46500	20100	13	42	44
Treatment 3	40	23300	9100	6	21	20
Treatment 4	50	33200	13200	7	30	29
Day 6						
Control	560	102900	38500	85	93	88
Treatment 1	50	32100	9600	7	29	21
Treatment 2	70	41000	20100	10	37	44
Treatment 3	20	21100	7800	3	19	17
Treatment 4	20	27700	11400	2	25	25

Peroxygen residuals in Soil 1 and Soil 2 for the four treatments over six days are listed in Tables 4-7 and 4-8, respectively. Some persulfate remained in the Treatment 1 and Treatment 3 systems after three days, but it decomposed to nondetectable after six days. Such rapid persulfate decomposition was likely driven by the generation of hydroperoxide in CHP reactions. Hydrogen peroxide was still present in systems containing phytate (Treatments 3 and 4) after six days, which denotes good potential for the distribution of hydrogen peroxide in the subsurface.

Table 4-7. Peroxygen Residuals in Soil 1 After Second Phase Treatments

Treatment	Hydrogen Peroxide (%)	Persulfate (%)
Day 3		
Treatment 1	Nondetectable	0.8%
Treatment 2	Nondetectable	N/A
Treatment 3	0.054%	1.1%
Treatment 4	0.054%	N/A
Day 6		
Treatment 1	Nondetectable	Nondetectable
Treatment 2	Nondetectable	N/A
Treatment 3	0.002%	Nondetectable
Treatment 4	0.005%	N/A

Table 4-8. Peroxygen Residuals in Soil 2 After Second Phase Treatments

Treatment	Hydrogen Peroxide (%)	Persulfate (%)
Day 3		
Treatment 1	Nondetectable	0.2%
Treatment 2	Nondetectable	N/A
Treatment 3	0.18%	0.5%
Treatment 4	0.08%	N/A
Day 6		
Treatment 1	Nondetectable	Nondetectable
Treatment 2	Nondetectable	N/A
Treatment 3	0.003%	Nondetectable
Treatment 4	0.002%	N/A

Third set of persulfate/peroxide reactions. Process conditions for the third phase of the treatability study are shown in Table 4-9 for Soil 1 and Table 4-10 for Soil 2. The goal of the third set of treatments was to investigate the effectiveness of a higher dosage of persulfate and a higher concentration of hydrogen peroxide for contaminant destruction. Contaminant residuals in Soil 1 for the six different treatments after three and six days of treatment are listed in Table 4-11. Control systems contained 85%–103% of the original contaminant concentrations.

Comparison of Treatments 1–3 (containing 4.5% persulfate) to Treatments 4–6 (CHP) showed minimal difference; i.e., the activity from oxidant generation from hydrogen peroxide was dominating that from oxidant generation from persulfate in the treatment of these soil–groundwater systems, and therefore it was proposed that CHP may provide a more economical means of treating the site. In both types of systems, greater contaminant destruction occurred with higher oxidant dosages.

Table 4-9. Process Conditions for Third Phase Treatments in Soil 1

Treatment 1	**Treatment 2**	**Treatment 3**
4.5% Sodium Persulfate 6% Hydrogen Peroxide 5 mM Phytate	4.5% Sodium Persulfate 9% Hydrogen Peroxide 5 mM Phytate	4.5% Sodium Persulfate 12% Hydrogen Peroxide 5 mM Phytate
Treatment 4	**Treatment 5**	**Treatment 6**
6% Hydrogen Peroxide 5 mM Phytate	9% Hydrogen Peroxide 5 mM Phytate	12% Hydrogen Peroxide 5 mM Phytate

Table 4-10. Process Conditions for Third Phase Treatments in Soil 2

Treatment 7	**Treatment 8**
4.5% Sodium Persulfate 12% Hydrogen Peroxide 5 mM Phytate	12% Hydrogen Peroxide 5 mM Phytate

Table 4-11. Residual Contaminants in Soil 1 After Third Phase Treatments

	Contaminant Residual (µg/L)			% Contaminant Remaining		
	TCE	Styrene	Ethylbenzene	TCE	Styrene	Ethylbenzene
Initial Conc.	170800	468900	8800	100	100	100
Day 3						
Control	162300	483000	8360	95	103	95
Treatment 1	88900	112600	2910	52	24	33
Treatment 2	73500	32900	1240	43	7	14
Treatment 3	80300	51600	1940	47	11	22
Treatment 4	92300	243900	3790	54	52	43
Treatment 5	85400	117300	1940	50	25	22
Treatment 6	104200	14100	440	61	3	5
Day 6						
Control	146900	459600	7480	86	98	85
Treatment 1	56400	89100	3080	33	19	35
Treatment 2	29100	42300	2030	17	9	23
Treatment 3	35900	51600	2380	21	11	27
Treatment 4	59800	75100	1240	35	16	14
Treatment 5	56400	150100	2820	33	32	32
Treatment 6	27400	136000	3880	16	29	44

Results of the treatment of Soil 2 with two process conditions are listed in Table 4-12. Similar to the results of Table 4-11, CHP was equally or more effective than CHP-activated persulfate for Soil 2.

Table 4-12. Residual Contaminants in Soil 2 after Third Phase Treatments

	Contaminant Residual (µg/L)			% Contaminant Remaining		
	TCE	Styrene	Ethylbenzene	TCE	Styrene	Ethylbenzene
Initial Conc.	650	110600	45500	100	100	100
Day 3						
Control	620	96300	43300	94	87	95
Treatment 7	450	15500	4100	69	14	9
Treatment 8	100	25500	8200	15	23	18
Day 6						
Control	590	102900	39590	90	93	87
Treatment 7	190	18900	4600	29	17	10
Treatment 8	40	16600	3700	5	15	8

Peroxygen residuals for Soil 1 and Soil 2 are listed in Tables 4-13 and 4-14, respectively. Hydrogen peroxide residuals were present in both soils after three days and also present after six days in Soil 2. As in the second phase of treatments, persulfate was consumed rapidly through decomposition by hydroperoxide, which is generated in CHP reactions.

Table 4-13. Peroxygen Residuals in Soil 1 After Third Phase Treatments

Treatment	Hydrogen Peroxide (%)	Persulfate (%)
Day 3		
Treatment 1	0.17	1.37
Treatment 2	0.04	0.11
Treatment 3	0.12	0.51
Treatment 4	0.10	N/A
Treatment 5	0.14	N/A
Treatment 6	0.08	N/A
Day 6		
Treatment 1	0.01	0.18
Treatment 2	Nondetectable	Nondetectable
Treatment 3	Nondetectable	0.03
Treatment 4	Nondetectable	N/A
Treatment 5	Nondetectable	N/A
Treatment 6	Nondetectable	N/A

Table 4-14. Peroxygen Residuals in Soil 2 After Third Phase Treatments

Treatment	Hydrogen Peroxide (%)	Persulfate (%)
Day 3		
Treatment 7	0.30	0.87
Treatment 8	0.41	N/A
Day 6		
Treatment 7	0.03	Nondetectable
Treatment 8	0.06	N/A

4.1.3 Summary

The peroxygen treatability study of the Michigan site showed that stand-alone CHP stabilized by phytate was equally effective as CHP-activated persulfate. And temperature rise was minimal in the phytate-CHP systems. Based on the array of process conditions evaluated, three injections of 9% hydrogen peroxide stabilized by 5 mM phytate was used for field implementation.

4.2 Gasoline Spill Treatability Study

4.2.1 Introduction

One subsurface solids sample and one groundwater sample collected from a gasoline spill in the Colorado Rocky Mountains were evaluated for potential full-scale treatment using CHP with the hydrogen peroxide stabilized by citrate and phytate. Additional data collection included peroxygen residuals and temperature changes.

4.2.2 Methodology

Hydrogen Peroxide Longevity and TPH Destruction. Hydrogen peroxide longevity studies were first conducted using 30 g of subsurface solids and 4 mL of hydrogen peroxide-stabilizer solution in 40 mL volatile organic analysis (VOA) vials. The 4 mL of hydrogen peroxide solution provided enough liquid to cover the solids plus approximately 2 mL with which to sample for hydrogen peroxide residuals. One hydrogen peroxide concentration (12%) and two stabilizers (sodium citrate at 1,500 mg/L and 3,000 mg/L and sodium phytate at 660 mg/L-1 mM, 1,320 mg/L-2 mM, and 3,300 mg/L-5 mM) were evaluated for hydrogen peroxide longevity. Control reactors received deionized water in place of hydrogen peroxide. The reactions were analyzed for hydrogen peroxide daily by iodometric titration. The reactions were allowed to proceed until the hydrogen peroxide was consumed. After the hydrogen peroxide was consumed, the entire reactor contents were extracted with methylene chloride and analyzed for TPH.

Hydrogen peroxide longevity was further optimized using a liquid:solid ratio more characteristic of the field (i.e., in which nearly all of the hydrogen peroxide is in contact with catalytic soil surfaces). Using 30 g of the subsurface solids, 2.5 mL of hydrogen peroxide solutions were added, and hydrogen peroxide was monitored at 1 day, 1.5 days, 2 days, 2.5 days,

and 3 days. Three hydrogen peroxide concentrations were evaluated (6%, 12%, and 18%) × three sodium phytate concentrations (0, 330 mg/L-0.5 mM, and 660 mg/L-1mM). The reactors were analyzed for total petroleum hydrocarbons (TPH) after the hydrogen peroxide was consumed.

4.2.3 Analyses

TPH concentrations were quantified on a Hewlett Packard 5890A gas chromatograph equipped with a flame ionization detector and a 30-m DB-1 capillary column. Chromatographic conditions included initial oven temperature of 40˚C, program rate of 10˚C/min, final temperature of 160˚C, injector temperature of 140˚C, and detector temperature of 180˚C. Peak areas for TPH in the extracts were compared to results of a standard curve prepared from unleaded dissolved in methylene chloride. Hydrogen peroxide concentrations were measured by iodometric titration. Temperature changes were measured using a mercury thermometer.

4.2.4 Results

Hydrogen peroxide lifetimes in Wolf Creek Pass spill solid-groundwater slurries with different stabilizer conditions are listed in Table 4-15. These results show that the phytate stabilized hydrogen peroxide systems provided enhanced hydrogen peroxide longevity relative to hydrogen peroxide only, and that hydrogen peroxide longevity increased with higher phytate dosages. The maximum hydrogen peroxide lifetime was 4 days with the addition of 3,300 mg/L of sodium phytate. Citrate stabilization of hydrogen peroxide was generally ineffective; the maximum lifetime of hydrogen peroxide was 1 day, which occurred at both concentrations of sodium citrate evaluated. This soil has excellent characteristics for applying hydrogen peroxide (related mainly to its mineralogy).

TPH destruction in the same reactors is listed in Table 4-16. TPH destruction was moderate, at 70% relative to control systems, in hydrogen peroxide only and in the reactors treated with 12% hydrogen peroxide stabilized by 660 mg/L phytate. TPH destruction increased with higher phytate concentrations; 95% TPH destruction was evident using 12% hydrogen peroxide and 3,300 mg/L sodium phytate. Addition of sodium citrate enhanced TPH destruction, but increased hydrogen peroxide decomposition. Previous studies conducted at the Chemical Oxidations Laboratory documented that citrate sometimes solubilizes metals sorbed to soils resulting in increased hydrogen peroxide decomposition.

In summary, adding the stabilizer sodium phytate increased the hydrogen peroxide longevity by one day (from 3 days to 4 days). More importantly, it provided conditions that resulted in greater TPH destruction (95% TPH destruction for stabilization with 3,300 mg/L sodium phytate vs. 70% TPH destruction with no stabilization).

Table 4-15. Hydrogen Peroxide Lifetimes in Systems under Different Conditions of Stabilization Using 4 mL Hydrogen Peroxide Solution/30 g of Subsurface Solids

Hydrogen peroxide conditions	Hydrogen Peroxide Longevity
12% H_2O_2	3 days
12% H_2O_2, 660 mg/L sodium phytate	3+ days
12% H_2O_2, 1320 mg/L sodium phytate	3+ days
12% H_2O_2, 3300 mg/L sodium phytate	4 days
12% H_2O_2, 1500 mg/L sodium citrate	1 day
12% H_2O_2, 3000 mg/L sodium citrate	1 day

Table 4-16. TPH Destruction in Systems under Different Conditions of Stabilization Using 4 mL Hydrogen Peroxide Solution/30 g of Subsurface Solids

Hydrogen peroxide conditions	TPH Destruction Relative to Control
12% H_2O_2	70%
12% H_2O_2, 660 mg/L sodium phytate	70%
12% H_2O_2, 1320 mg/L sodium phytate	93%
12% H_2O_2, 3300 mg/L sodium phytate	95%
12% H_2O_2, 1500 mg/L sodium citrate	98%
12% H_2O_2, 3000 mg/L sodium citrate	95%

A second round of studies was conducted with slightly more than one pore volume of groundwater mixed with hydrogen peroxide and stabilizer. The volume of solution added was 2.5 mL/30 g of soil, which provide just enough extra volume to sample for hydrogen peroxide (The first round of evaluations were conducted using 4.0 mL of solution/30 g of soil.) This second round of study provided the most realistic laboratory conditions that can be related to the field; i.e., all of the hydrogen peroxide solution was in contact with mineral surfaces (which are the primary catalysts for hydrogen peroxide decomposition). The results of the second round of testing are listed in Table 4-17. Hydrogen peroxide lifetimes increased with higher hydrogen peroxide concentrations because of the higher mass of hydrogen peroxide; the higher the initial mass of hydrogen peroxide, the longer the time required for the mass to decompose. In addition, hydrogen peroxide lifetimes increased with higher phytate concentrations. TPH destruction increased with both higher hydrogen peroxide concentrations and phytate concentrations. Temperature increases in these samples were negligible (Table 4-17); there was no temperature rise in any of the tests with the exception of 18% hydrogen peroxide without stabilization. In this system, the temperature rose from 22˚C to 28˚C. These results confirm that hydrogen peroxide addition to these soils does not provide a threat of high temperature, exothermic reactions.

Table 4-17. Hydrogen Peroxide Lifetimes and TPH Destruction in Subsurface Systems under Different Conditions of Stabilization Using 2.5 mL Hydrogen Peroxide Solution/30 g of Subsurface Solids

Treatment	Percent TPH Destruction	Hydrogen Peroxide Longevity	Maximum Temperature (˚C)
6% H_2O_2	71%	1 day	22
6% H_2O_2 + 330 mg/L Phytate	70%	1 day	22
6% H_2O_2 + 660 mg/L Phytate	76%	1 day	22
12% H_2O_2	88%	1.5 days	23
12% H_2O_2 + 330 mg/L Phytate	85%	2 days	22
12% H_2O_2 + 660 mg/L Phytate	92%	2 days	22
18% H_2O_2	98%	2 days	28
18% H_2O_2 + 330 mg/L Phytate	98%	2.5 days	22
18% H_2O_2 + 660 mg/L Phytate	98%	2.5 days	22

4.2.5 Summary and Recommendation

A subsurface solid-groundwater sample collected from a gasoline spill site was evaluated for in situ treatment using catalyzed H_2O_2 propagations (CHP). Hydrogen peroxide dosages varied from 6% to 18%, and sodium citrate and sodium phytate were evaluated as stabilizers of hydrogen peroxide. The most effective TPH destruction was with 12% hydrogen peroxide and 3,300 mg/L sodium phytate and with 18% hydrogen peroxide and 330 mg/L sodium phytate. The use of 18% hydrogen peroxide is somewhat higher than normal. Most vendors use a maximum of 12% hydrogen peroxide. However, this soil is so unreactive that the vigorous hydrogen peroxide decomposition seen in most hydrogen peroxide-soil systems does not occur in this system. There was no temperature rise in any of the tests with the exception of 18% hydrogen peroxide without stabilization. In this system, the temperature rose from 22˚C to 28˚C. Use of 18% hydrogen peroxide with stabilization by 330 mg/L sodium phytate should provide effective treatment at the spill site.

5 References

Afanas'ev, I.B., 1989. Superoxide Ion: Chemistry and Biological Implications, Vol.1. CRC Press, Boca Raton, FL.

Borden, R.C., 2010. Development of Design Tools for Planning Aqueous Amendment Injection Systems (ESTCP Project ER-200626). Environmental Security Technology Certification Program, Arlington, VA.

Buxton, G.V., Greenstock, C.L., Helman, W.P., Ross, A.B., 1988. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (•OH/•O^-) in aqueous solution. J. Phys. Chem. Ref. Data, 17, 513-780.

Baciocchi, R., Boni, M. R., D'Aprile, L., 2004. Application of H_2O_2 lifetime as an indicator of TCE Fenton-like oxidation in soils. J. Hazard. Mater. B107, 97-102.

Chang, P.B.L., Young, T.M. 2000. Kinetics of methyl tert-butyl ether degradation and by-product formation during UV/hydrogen peroxide water treatment. Water Res. 34(8), 2233-2240.

Corbin, J.R., Teel, A.L., Allen-King, R.M., Watts, R.J., 2007. Reductive oxygen species responsible for the enhanced desorption of dodecane in modified Fenton's system. Water Environ. Res. 79(1), 37-42.

David, M.D., Seiber, J. N., 1999. Accelerated hydrolysis of industrial organophosphates in water and soil using sodium perborate. Environ. Pollut. 105(1), 121-128.

Edwards, J.O., Pearson, R.G., 1962. The factors determining nucleophilic reactivities. J. Am. Chem. Soc. 84, 16-24.

ESTCP (Environmental Security Technology Certification Program), 1999. Technology Status Review: In Situ Oxidation. Environmental Security Technology Certification Program, Arlington, VA.

Furman, O.S., Laine, D.F., Blumenfeld, A., Teel, A.L., Shimizu, K., Cheng, I.F., Watts, R.J., 2009. Enhanced reactivity of superoxide in water-solid matrices. Environ. Sci. Technol. 43(5), 1528-1533.

Gavaskar, A., Gupta, N., Sass, B., Janosy, R., Hicks, J., 2000. Design guidance for application of permeable reactive barriers for groundwater remediation. Final Report to the Air Force Research Laboratory, Tyndall Airforce Base, FL.

Haag, W.R., Yao, C.C.D., 1992. Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. Environ. Sci. Technol. 26, 1005-1013.

Hinchee, R.E., Downey, D.C., Aggarwal, P.K., 1991. Use of hydrogen peroxide as an oxygen source for in situ biodegradation: Part I. Field studies. J. Hazard. Mater. 27, 287-299.

Hui, Y. 2001. Mechanisms of Fenton-like reactions for reduction of refractory organic compounds. Ph.D. Dissertation. Washington State University. 121p.

Huling S.G., Arnold R.G., Sierka R.A., Miller M.R., 2001. Influence of peat on Fenton oxidation. Water Res. 35, 1687-1694.

Interstate Technology & Regulatory Council (ITRC), 2001. Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater. Interstate Technology & Regulatory Council, Washington, D.C.

Interstate Technology & Regulatory Council (ITRC), 2005. Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater, Second Edition. Interstate Technology & Regulatory Council, Washington, D.C.

Miller, C.M., Valentine, R.L., 1995. Hydrogen peroxide decomposition and quinoline degradation in the presence of aquifer material. Water Res. 29, 2353-2359.

Pignatello, J.J., Baehr, K., 1994. Waste management: ferric complexes as catalysts for "Fenton" degradation of 2,4-D and metolachlor in soil. J. Environ. Qual. 23, 365-369.

Ravikumar, J.X., Gurol, M., 1994. Chemical oxidation of chlorinated organics by hydrogen peroxide in the presence of sand. Environ. Sci. Technol. 28, 394-400.

Schmidt, J.T., Ahmad, M., Teel, A.L., Watts, R. J., 2011. Hydrogen peroxide stabilization in one-dimensional flow columns. J. Contam. Hydrol. 126, 1-7.

Schmelling, D.C., Gray, K.A., Kamat, P.V. 1998. Radiation-induced reactions of 2,4,6-trinitrotoluene in aqueous solution. Environ. Sci. Technol. 32(7), 971-974.

Schnarr, M., Farquhar, G. 1992. An in situ oxidation technique to destroy residual DNAPL from soil. Subsurface Restoration Conference, Third International Conference of Ground Water Quality. Dallas, Texas, Jun 21-24, 1992.

Sheldon, R.A., J.K. Kochi. 1981. Metal-catalyzed reactions of organic compounds: Mechanistic principles and synthetic methodology including biochemical processes. Academic Press. New York, NY.

Smith, B.A., Teel, A.L., Watts, R.J., 2004. Identification of the reactive oxygen species responsible for carbon tetrachloride degradation in modified Fenton's systems. Environ. Sci. Technol. 38, 5465-5469.

Smith, B.A., Teel, A.L., Watts, R.J., 2006. Destruction of carbon tetrachloride and chloroform DNAPLs by modified Fenton's reagent. J. Contam. Hydrol., In Press.

Sun, Y., Pignatello, J. J., 1992. Chemical treatment of pesticide wastes. Evaluation of Fe(III) chelates for catalytic hydrogen peroxide oxidation of 2,4-D at circumneutral pH. J. Agric. Food Chem. 40, 322-327.

Teel, A.L., Watts, R.J., 2002. Degradation of carbon tetrachloride by Fenton's reagent. J. Hazard. Mater. B94(2), 179-189.

Tyre, B.W., Watts, R.J., Miller, G.C., 1991. Treatment of four biorefractory contaminants in soils using catalyzed hydrogen peroxide. J. Environ. Qual. 20(6), 832-888.

U.S. DOE, 1999. Innovative Technology Summary Report: Fenton's Reagent (DOE/EM-0484). Office of Science and Technology, Washington, D.C.

Walling, C., 1975. Fenton's reagent revisited. Acc. Chem. Res. 8, 125-131.

Watts, R.J. 1998, Hazardous Wastes: Sources, Pathways, Receptors. John Wiley & Sons, New York.

Watts, R. J., Bottenberg, B. C., Hess, T. F., Jensen, M. D., Teel, A. L., 1999. Mechanism of the enhanced treatment of chloroaliphatic compounds by Fenton-like reactions. Environ. Sci. Technol. 33, 3432-3437.

Watts, R.J., Finn, D.D., Cutler, L.M., Schmidt, J.T., Teel, A.L., 2007. Enhanced stability of hydrogen peroxide in the presence of subsurface solids. J. Contam. Hydrol. 91, 312-326.

Watts, R.J., Kong, S., Dippre, M., Barnes, W.T. 1994. Oxidation of sorbed hexachlorobenzene in soils using catalyzed hydrogen peroxide. J. Hazard. Mater., 39, 33-47.

Watts, R.J., Sarasa, J., Loge, F.J., Teel, A.L., 2005. Oxidative and reductive pathways for contaminant degradation in the manganese-catalyzed decomposition of hydrogen peroxide. J. Environ. Eng. 131, 158-164.

Watts, R.J., Teel, A.L., 2005. Chemistry of modified Fenton's reagent (catalyzed H_2O_2 propagations—CHP) for *in situ* soil and groundwater remediation. J. Environ. Eng. 131, 612-622.

Watts, R.J., Teel, A.L., 2006. Treatment of contaminated soils and groundwater using ISCO. Pract. Period. Hazard. Tox. Radio. Waste Manag. 10(1), 2-9.

Watts, R.J., Udell, M.D., Monsen, R.M., 1993. Use of iron minerals in optimizing the peroxide treatment of contaminated soils. Water Environ. Res. 65, 839-845.

Watts, R. J., Udell, M. D., Rauch, P. A., Leung, S. W., 1990. Treatment of pentachlorophenol-contaminated soils using Fenton's reagent. Hazard. Wastes Hazard. Mater. 7(4), 335-345.

Yeh, C. K.-J., Wu, H.-M., Chen, T.-C., 2003. Chemical oxidation of chlorinated non-aqueous phase liquid by hydrogen peroxide in natural sand systems. J. Hazard. Mater. 96, 29-51.

Zhong, L., Szecsody, J., Oostrom, M., Truex, M., Shen, X., Li, X., 2011. Enhanced remedial amendment delivery to subsurface using shear thinning fluid and aqueous foam. J. Hazard. Mater. 191, 249-257.

Appendices

Appendix A: Contact Information

Washington State University

Richard J. Watts (Principle Investigator (PI)), Washington State University, Pullman, WA, 99163-2910, phone: (509) 335-3761, fax: (509) 335-7632, e-mail rjwatts@wsu.edu

Amy Teel, Washington State University, Pullman, WA, 99163-2910, e-mail amy_teel@wsu.edu

ERM

Dick Brown, 250 Phillips Blvd., Suite 280, Ewing NJ 08618, Direct Dial: 609-403-7530, Office Phone: 609-895-0050, Cell 609-647-4119, Fax: 609-895-0111 e-mail dick.brown@erm.com

Rick Lewis, 399 Boylston Street, 6th Floor, Boston, MA, 02116, USA, (617) 646-7863, rick.lewis@erm.com

Tim Pac, 171 Forbes Blvd., Suite 5000, Mansfield, MA 02048, (617) 646 7862 Fax: (508) 261 7777, Mobile: (617) 285 4466, tim.pac@erm.com